ENERGETIC MATERIALS

Volume 1: Physics and Chemistry of the Inorganic Azides
Volume 2: Technology of the Inorganic Azides

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Physics and Chemistry of the Inorganic Azides

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and b + i. Some of the reactions are evidently complex, and such equations given later in the text are not strictly quantitative.

Curtius discovered HN_3 [1] by reacting benzoylhydrazine with nitrous acid (b + g-type reaction). The resulting benzoyl azide was saponified, and sodium azide was isolated from the alkaline mixture. In 1903 Wislicenus [14] synthesized sodium azide solely from inorganic compounds, namely, sodium metal, ammonia, and dinitrogen oxide (a + e). The reaction proceeds in two steps, first converting ammonia with sodium to sodamide, and then reacting this with dinitrogen oxide to yield sodium azide. Fifty percent of the sodamide is decomposed to hydroxide and ammonia, and the overall balance of the process is

$$2NaNH_2 + N_2O \longrightarrow NaN_3 + NaOH + NH_3$$

Wislicenus conducted the synthesis as a dry procedure at elevated temperature; a low-temperature procedure in liquid ammonia was later patented by Acken and Filbert [15]. Although inherently only 50% effective, both versions have otherwise excellent yields and are now almost exclusively used for the manufacture of sodium azide.

Darapsky [16] synthesized azide by oxidizing hydrazodicarbonamide with hypochlorite, an (a + b) reaction with both nitrogen species in the same molecule. Hydrazine, also discovered by Curtius, is the starting material in several other azide syntheses. One of these processes, independently invented by Thiele [17] and Stolle [18] and patented by the latter, uses nitrous acid or nitrites as an oxidant (b + g reaction type):

$$N_2H_4 + NOOH \longrightarrow HN_3 + 2H_2O$$

The process is carried out in alkaline media with alkyl nitrite and yields 80% sodium or potassium azide. It was for decades competitive with Wislicenus' method for commercial azide production. Unnoticed at the time, this azide retains small amounts of hydrazine as an impurity, which was later found to be indispensable for azidation reactions in organic chemistry ("active" sodium azide).

In another approach, Angeli [19] oxidized hydrazine with silver nitrite to precipitate silver azide:

$$N_2H_4 + AgNO_2 \longrightarrow AgN_3 + 2H_2O$$

For lecture demonstrations, Curtius [20] recommended the mixing of hydrazine with liquefied N_2O_3, and Dennstedt and Göhlich [21] improved the yield of the method by working in strongly acid media.

Other syntheses with hydrazine have low yields and may produce azide as a side reaction, such as the approach of Sabaneyev [22] who used nitric acid (a + i) as an oxidant. In another approach, Tanatar [23] reacted hydrazine and nitrogen trichloride (b + a):

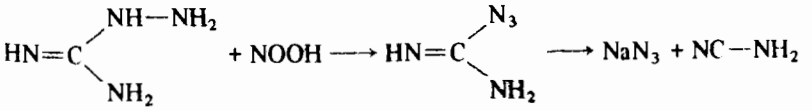
$$N_2H_4 + NCl_3 \longrightarrow HN_3 + 3HCl$$

The same author [24] also obtained HN_3 from hydrazine and hydroxylamine by oxidation (b + c):

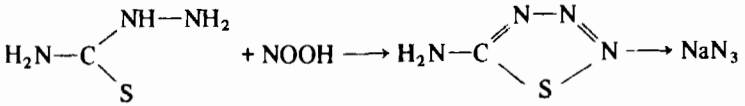
$$N_2H_4 + NH_2OH + 2O \longrightarrow HN_3 + 3H_2O$$

Of various oxidants tested, hydroperoxide and chromic acid gave the best results (24% yield).

Thiele [25] converted aminoguanidine with nitrous acid (b + g) to guanyl azide [26] which was saponified to sodium azide:



Another interesting reaction (b + g) was studied by Freund and Schander [27]. Thiosemicarbazide was reacted with nitrous acid to yield 5-aminothiatriazole which was then saponified to yield sodium azide:



Browne found [28] that the oxidation of hydrazine alone leads to HN_3 in strongly acid media. The yields ranged from 19 to 29%.

Direct synthesis of HN_3 from the elements has also been explored [29], but the yields were minimal.

With the advent of commercial sodium azide, most of the above methods have gradually disappeared from the laboratory. Only the Wislicenus and, occasionally, the Thiele processes are still in use.

E. PREPARATION OF HN_3

1. Hydrogen Azide

Hydrogen azide is a colorless liquid (MP, -80°C [30]; BP, +37°C [31]) which is toxic and very sensitive; it should be handled with great caution. Curtius and Radenhausen [31] reported two typical accidents. In the first instance, an explosion occurred when the substance was introduced into a barometer vacuum chamber: "The blast of 50 mg was sufficient to disintegrate the apparatus to dust and spew the mercury in finest distribution into the remotest corners of the very large room." In the second accident, Radenhausen was seriously injured when "approximately 700 mg HN_3 exploded spontaneously when the vessel containing it was removed from a cooling bath, with the shock shattering every glass vessel nearby."

In general, it can be said that gaseous hydrogen azide will invariably explode when thermally shocked or when sudden pressure changes occur. The gas may

also explode spontaneously at normal or increased pressures. The tendency cannot be controlled; hence, hydrogen azide gas must be handled at reduced pressure or diluted with an inert gas.

Liquid hydrogen azide also explodes on thermal or mechanical shock [31]. The freshly prepared liquid reportedly does not explode spontaneously, but tends to do so upon aging [31]. Solid hydrogen azide explodes likewise on thermal and mechanical shock; spontaneous explosions are not reported.

There are several methods for making hydrogen azide, which are all based on the simple equation

$$NaN_3 + H^+ \longrightarrow HN_3 + Na^+$$

Sodium azide, at elevated temperature, is reacted with a suitable acid, and gaseous hydrogen azide is evolved. The acid must not chemically attack the azide ion, and the reactants must be less volatile than HN_3. Suitable acids are sulfuric, phosphoric, phosphorous, oxalic, perchloric, fluosilicic, stearic, and palmitic acids.

Smaller quantities may be prepared from solid sodium azide and half-concentrated sulfuric acid in a 250-ml round flask, fitted with gas inlet and outlet tubes and a dropping funnel. Up to 5 g sodium azide are placed in the flask and heated to 80°C. The acid is then added dropwise, while a stream of nitrogen passes through to carry the hydrogen azide vapors through a drying tube (calcium chloride) into a cold trap (liquid nitrogen) fitted with another drying tube at the outlet [30].

The use of concentrated sulfuric acid in this process would eliminate water, but is not recommended as some reaction with the azide is inevitable, leading to impurities such as hydroxylamine [32] and sulfur dioxide [33]. If concentrated H_2SO_4 is chosen, the procedure should be conducted *in vacuo*, the gases passed onto a cold finger, and the deposit allowed to warm up to remove the lower boiling impurities [34].

Air [35] and hydrogen [36] have also been used as carriers. To prevent explosions, the ratio of carrier to hydrogen azide should be 10 or more [37]. Seel *et al.* [38] made specified quantities of hydrogen azide by generating the gas without carrier *in vacuo* and expanding it into a large flask filled with vacuum-dried calcium chloride. After several hours, the dry gas was expanded into gas ampoules of known volume and measured via pressure and temperature.

When larger batches of HN_3 are to be generated, clogging of the drying tower may be expected with the disastrous consequences of a pressure build-up. Reitzner and Manno [39] recommended, therefore, the addition of the desiccant to the reaction mixture, thus avoiding the necessity of drying the final product. According to

$$H_3PO_4 + NaN_3 \xrightarrow{P_2O_5} HN_3 + NaH_2PO_4$$

the reaction vessel was charged with phosphoric acid, saturated with phosphorus pentoxide. At 100–120°C pot temperature a 5 M sodium azide solution was added dropwise while nitrogen passed through the system. The water from the azide solution was bound by the pentoxide and the gas mixture passed through a reflux condenser merely to remove phosphoric acid droplets. In the experience of others [37], the above method yields initially a dry HN_3 product, but increasing formation of polyphosphoric acids decelerates the water absorption, and subsequent drying of the gas becomes necessary. Preference should, therefore, be given to the elegant method of Guenther and Meyer, which employs dry sodium azide and a low-melting acid, such as stearic or palmitic acids, thus avoiding any water or other solvent in the process:

$$NaN_3 + CH_3(CH_2)_{16}COOH \longrightarrow HN_3 + CH_3(CH_2)_{16}COONa$$

stearic acid, MP 69.9°C

The original synthesis [40] was conducted in a vacuum line without carrier gas, using 25 g, carbonate-free, dry sodium azide, and 100 g stearic acid in a 500-ml reaction vessel heated to 80–90°C. The mixture melted and developed HN_3 gas slowly and steadily. The reaction rate was controlled by regulating the temperature and ceased immediately when the mixture froze. The gas was then condensed in a trap at -40°C.

The stearic acid method may be scaled up or, at a slightly higher temperature, used at normal pressure with a carrier gas. In either case, the unspent, frozen reaction mixture may be reused.

Engler and Kohlrausch [41] made milligram quantities of hydrogen azide in a similar dry process with phosphorus acid (MP, 26.5°C):

$$NaN_3 + H_3PO_3 \longrightarrow HN_3 + NaH_2PO_3$$

Thrush [42] made small amounts of hydrogen azide by bubbling nitrogen through an aqueous hydrazoic acid solution; the gases were dried with P_2O_5.

In an attempt to produce hydrogen azide with a volatile acid, hydrochloric acid gas was at room temperature passed through a column packed with dry sodium azide; the method reportedly [33] gave a poor yield, and hydrogen chloride had to be removed from the product.

2. Deuterium Azide

Deuterium azide, DN_3, was made from deuterophosphoric acid and sodium azide, either by dropping the acid onto the azide [43,44], or by adding dropwise a solution of sodium azide in deuterium oxide to the deuterophosphoric acid [45]. The Guenther-Meyer reaction, using deuterostearic acid, was also used [46].

3. Aqueous Hydrazoic Acid Solutions

Concentrated solutions of hydrazoic acid are not safe to handle as they explode on mild mechanical shock and may also explode spontaneously. Dilute

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solutions of 10% or less involve no explosion hazards. Nevertheless, hydrazoic acid is highly volatile and rather toxic (it is pharmacologically defined as a potent hypotensive drug), and since it is rarely handled in closed systems, intoxication may occur by breathing its vapors. First indication of the physiological effect is a distinct reddening of the eyeballs, followed by nasal congestion and increased heart frequency. Hence, the use of a fume hood is indispensible, and it is also good practice to have a mirror in the working area. Fortunately, HN_3 has a distinct, pungent odor, and the toxic effect is noncumulative. For further details on safety and first aid, see Chapter 3 in Volume 2.

Like hydrogen azide, the aqueous hydrazoic acid solutions are made by decomposing sodium azide with an acid, which is followed by separating the product by any of the following methods. One of them [47,48] makes use of the volatility of HN_3 with water vapors:

$$NaN_3 + H_2SO_4 \longrightarrow HN_3 + NaHSO_4$$

Sodium azide (15 g) is dissolved in 150 ml water and placed in a flask fitted with a dropping funnel and a Liebig condenser; the receiver contains 100 ml water. After the solution has been brought to boil, 90 ml sulfuric acid (40%, v/v) is added dropwise. To obtain a 3% hydrazoic acid, distillation is continued until 50 ml remains in the flask. It is important to add the acid to the already boiling solution, as otherwise concentrated hydrazoic acid vapors build up in the reaction flask and cause explosion.

Larger amounts of hydrazoic acid may be routinely prepared as follows [37]. The generator consists of a 4-liter reaction flask, containing a large magnetic stirring bar, and is fitted with a sealed gas-inlet tube, dropping funnel, thermometer well, and a reflux condenser with a Teflon tube to the receiver. Sealed glass connections are essential, because ground joints were found to explode when opened after prolonged periods of use, evidently because HN_3 penetrated into the lubricant to form a friction-sensitive mixture. Teflon tubing is superior to vinyl as the latter becomes brittle in time and contaminates the product with an oily liquid. The flask is filled through the gas-inlet tube with one third its volume of 85% phosphoric acid. After heating to 100°C, the acid is vigorously stirred and a 4 M sodium azide solution added dropwise while nitrogen gas passes through the generator. It is necessary to maintain a carrier gas/hydrazoic acid ratio of at least 10:1 to avoid spontaneous explosions. Optimal temperature of the liquid phase is 100–120°C. The outgoing gas mixture may be directly passed over metal substrates to produce thin azide films or bubbled into water or metal hydroxide solution to make hydrazoic acid or metal azides, respectively.

Vaporization of the HN_3 can be avoided by selecting acids that have insoluble sodium or potassium salts, and the hydrazoic acid is then separated by filtration. This procedure is safer than the distillation methods; however, purity is sacrificed as the product is inherently contaminated. A number of reaction mixtures have been recommended [49], (Table IV). With the first reactant

Table IV. Preparation of Hydrazoic Acid via Precipitation

Reaction pair	By-product	Solubility of by-product: Percent (w/w)	Solubility of by-product: Temp. (°C)
Sodium azide + fluosilicic acid	Sodium fluosilicate	0.5	0
Potassium azide + fluosilicic acid	Potassium fluosilicate	0.2	0
Potassium azide + perchloric acid	Potassium perchlorate	0.75	0
Sodium azide + oxalic acid	Sodium hydrogen oxalate	1.7	15

pair of Table IV, the process is conducted as follows:

$$2NaN_3 + H_2SiF_6 \longrightarrow 2HN_3 + Na_2SiF_6$$

To an ice cold solution of 10 g sodium azide in 100 ml water, 41 g of a 27% fluosilicic acid are added. Sodium fluosilicate precipitates, and the filtered solution contains 6.6 g hydrazoic acid, contaminated with 0.7 g fluosilicate [49].

Explosion hazards associated with elevated temperatures and concentrated solutions or vapors of HN_3 are also avoided when hydrazoic acid is made by ion exchange. Both anion or cation exchange would work in principle but, for reasons to be discussed later, the former reaction type is not practical. The cation exchange, conducted either in a column or as batch process, is in essence a metathetical reaction between a strongly acidic resin (Rc—H) in its hydrogen form and sodium azide, but is obviously superior to the above-mentioned

$$Rc{-}H + NaN_3 \longrightarrow Rc{-}Na + HN_3$$

precipitations as the resin as a stationary, insoluble phase does not contaminate the product. Some other features of a more speculative nature have been claimed for the method; namely, that [50]:

1. A chemically pure product is obtained even with technical grade sodium azide, because the method removes cation impurities.
2. The resin has a naturally built-in indicator to indicate exhaustion.
3. The concentration of the hydrazoic acid obtained equals that of the eluent and choice may be given up to a 20% concentration.

These claims are not realistic [51–53]; indeed, although certain cation impurities are removed from sodium azide, it contains foreign anions that are carried through. Also, the exchange resins themselves contain cation impurities, notably iron and copper, which are complexed and eluted as anionic azido complexes, thus introducing new impurities. One of them is the "built-in" red indicator, namely, azidoiron anions. Their chemical composition and retention on the resin, however, depend on the ionic strength (concentration) of the eluent, and elution at the point of proton exhaustion would be coincidental.

Matching concentrations of eluent and effluent are not obtained, because the latter is inherently diluted by the wet resin through diffusion, an effect that is

particularly noticeable in the column technique. Moreover, a dilution of the product is unavoidable, particularly in the batch technique, due to the extreme volatility of HN_3; thus, although quantitative exchange may be assumed, the practical yields are only between 60 and 90%. In concentrations above 1 molar, hydrazoic acid begins to break down the resin, and this together with its volatility practically limits the preparation by ion exchange to concentrations up to 1 molar.

In anion exchange, hydrazoic acid would be made by eluting a basic resin in its azide form ($Ra—N_3$) with a suitable acid:

$$Ra—N_3 + HClO_4 \longrightarrow Ra—ClO_4 + HN_3$$

Besides being wasteful to make, however, azide resins are not stable, developing gas pockets upon storage, and, in turn, releasing alkylamines into the effluent.

In summary, aqueous hydrazoic acid solutions up to 1 molar are conveniently made by cation exchange and are obtained chemically pure from anion pure (nitrate) sodium azide and a prepurified resin. Purification of the latter by washing the heavy metals out as chloro complexes is simple in principle, but time-consuming. For projects requiring numerous hydrazoic acid batches the approach has its advantages, but for single preparations distillation methods are preferable.

The column technique proceeds as follows [53]: The column of 24-mm ID is filled with 350 ml (= 665 milliequivalents) of the wet cation exchange resin of strongly acidic type [for example, Amberlite IR-120(H)-AR] in its hydrogen form. Transition-metal impurities are first removed by rinsing the column with two bed-volumes each of 0.5 N, 2 N, 4 N, 6 N, 8 N, and concentrated hydrochloric acid, followed by water until chloride free, and 150 ml of 2 M sodium azide solution (= 350 milliequivalents). When the latter has been absorbed by the resin (which shrinks somewhat during the process), the exchange is completed with 800 ml water. To obtain a 0.5 M hydrazoic acid (= 2%), the first 150 ml effluent is discarded, and the following 500 ml collected. Or, a 1 M acid (= 4%) is obtained by discarding the first 200 ml and collecting the following 200 ml. In either case, subsequent fractions contain hydrazoic acid of decreasing concentration.

For the batch technique [50], a 10% sodium azide solution is poured into a beaker containing the moist resin in its hydrogen form. After stirring for several minutes, the hydrazoic acid is decanted. The amount of sodium azide used should not exceed one half the exchange capacity of the resin.

4. Nonaqueous Solutions of Hydrazoic Acid

One of the more frequently used solvents for hydrazoic acid is ethyl ether. If a small water content (approximately 1%) can be tolerated, an aqueous solution of HN_3 may be extracted with ether in a separatory funnel. Such an

ethereal solution may be further dried by adding calcium chloride or sodium sulfate, but due to the high volatility of both ether and HN_3, the operation is cumbersome unless only small quantities are made. It is, therefore, usually better to add, for example [54], 5 g pulverized sodium azide in small portions to a cooled mixture of 100 ml ether and 2 ml concentrated sulfuric acid and filter off the precipitated sodium bisulfate.

Larger amounts are made in a distillation process [47,48]. A 500-ml flask fitted with a dropping funnel and a descending condenser contains 65 g (1 mole) of azide; the receiver contains 200 ml ice cold ether. The flask is then charged with 200 ml water and 200 ml ether, and 60 ml concentrated sulfuric acid is added dropwise beneath the surface. Due to the heat of reaction, most of the hydrazoic acid distills together with ether vapors; the rest is distilled with gentle heating. The resulting solution may be dried with calcium chloride and then redistilled.

Solutions of hydrazoic acid in methanol are obtained by bubbling an air/hydrazoic acid mixture into dry methanol; for example [55], using a 250-ml flask, hydrazoic acid vapor from 10 g sodium azide and sulfuric acid is mixed with a stream of air, and the vapors are absorbed in −40°C methanol (200 ml) within 90 min.

Chloroform solutions are made by covering a slurry of equal parts sodium azide and water with three parts chloroform; the mixture is cooled to 0°C. Concentrated sulfuric acid (one equivalent for two of sodium azide) is added to this between 0 and +10°C. The solution is then decanted and dried over sodium sulfate [56].

Similarly, sodium azide may be placed under carbon tetrachloride to be decomposed with concentrated sulfuric acid [57]; the carbon tetrachloride solution is then decanted. Alternatively, sodium azide and the tetrachloride are treated in a separatory funnel with diluted (*d*, 1.5) phosphoric acid [58].

The above technique for chloroform may also be used for benzene and xylene solutions of hydrazoic acid [56], unless the following, somewhat more elaborate, method is used: 70 g pulverized sodium azide is placed in a beaker containing 500 ml dry benzene. The exact amount of HCl gas, made by decomposing 58 g sodium chloride with concentrated sulfuric acid, is bubbled into the vigorously stirred azide suspension. The liquid is then stirred until chloride-free and filtered. Due to some evaporation of hydrazoic acid, the solution is 6–7% concentrated (theoretically 8%) [59].

Nonaqueous solutions of deuterazoic acid have also been reported in the literature. For example to prepare a solution in chloroform, 2 g sodium azide was dissolved in deuterium oxide. To this was added a solution of 1.2 g deuterophosphoric acid (85% w/w in deuterium oxide), and the mixture was extracted five times with 20 ml chloroform [60]. A different approach was used to make a carbon tetrachloride solution of deuterazoic acid [57]: A solution of hydrazoic acid in carbon tetrachloride as prepared above was shaken with deuterium oxide, resulting in a 75–80% conversion to deuterazoic acid.

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F. AZIDES OF THE IA METALS

All azides of the group IA metals are available from commercial sources, but they are not sufficiently pure for many research tasks and hence are frequently prepared or at least purified in the laboratory. The reactions may be conducted in aqueous media; additional methods in nonaqueous media are available specifically for lithium azide, making use of the solubility of this salt in organic liquids (Table V). The azides of the group are typical monovalent alkali metal salts with metal-to-azide bonds of 60% ionic character in lithium azide, 67% in sodium azide, 70% in potassium and rubidium azides, and 74% in cesium azide. Together with the heavier IIA azides (calcium and strontium azides, 63% ionic; and barium azide, 67%), they are usually referred to as the ionic azides. Explosion hazards under laboratory conditions are negligible in group IA. Lithium azide, as the most sensitive compound, explodes with a 50% probability upon impact of a 2-kg weight dropping from 108 cm [61].

1. Lithium Azide

Lithium azide, LiN_3, is a white, hygroscopic, water-soluble salt (solubility, 37.4% w/w at 0°C, 40.1 at 20°C, and 48 at 68.2°C). A tetrahydrate is stable below -31°C, a monohydrate between -31 and +68°C, and an anhydric form above 68°C [35]. At room temperature the monohydrate may be dehydrated in high vacuum or over phosphorus pentoxide. Unlike the other IA azides, LiN_3 dissolves readily in alcohol (16.9% at 0°C) and in hydrazine (16% at room temperature, 23% at 50°C). Both the anhydric and monohydric forms explode on thermal shock above 115°C; slow heating delays the explosion to about 298°. The anhydric form has found frequent use as an azidation agent for making other azides, such as nitryl azide [64,65], boron azide halides [66-70], and various metalorganic azides [71,72].

Aqueous solutions of lithium azide are obtainable in various ways (Table V). For example, barium azide is reacted with lithium sulfate to precipitate barium sulfate, which is filtered off [62,73]; the product is, however, contaminated with either sulfate or lithium. More directly, hydrazoic acid may be neutralized with lithium hydroxide [74-78] or carbonate [74,80]. Or, a cation exchange resin in its lithium form is eluted with sodium azide [81]. All of these methods yield dilute solutions which are first concentrated to incipient crystallization; the final crystallization is best achieved in a vacuum desiccator [80]. The crude product is either recrystallized from dilute hydrazoic acid or dissolved in alcohol and precipitated with ether [79]. Precipitation from aqueous solutions with alcohol has also been recommended [75], apparently without realizing that over 80% of the azide remains in solution.

The above preparations in aqueous media incorporate some unavoidable hydrolytic decomposition (therefore recrystallization from hydrazoic acid), which is reduced in alcohol media. For example, lithium chloride [82] may be reacted with sodium azide in absolute alcohol:

$$LiCl + NaN_3 \longrightarrow LiN_3 + NaCl$$

Of the four salts involved, lithium azide has the highest solubility in alcohol and stays in solution. A solution of 8.5 g (0.5 mole) of lithium chloride in 200 ml ethanol is admixed to 13 g (0.5 mole) of sodium azide in 30 ml hot water. After agitating for 10 min, the mixture is filtered and the filtrate containing the lithium azide is evaporated to obtain white crystals. The crude product, containing sodium azide and chloride, is extracted with five times its weight of ethanol. After filtering, nine volumes of ether are added to precipitate pure lithium azide. The process yields 92% crude and 71% fine product [49]. As a variation, 8.5 g lithium chloride is dissolved in 200 ml methanol and refluxed for 5 hr with 15 g solid sodium azide. After filtration, the lithium azide solution is suitable for organic azidation reactions. Lithium sulfate may be used as the starting compound for either variation [83]. The preparation can also be accomplished from lithium organic compounds in water-free solvent:

$$LiC_4H_9 + HN_3 \longrightarrow LiN_3 + C_4H_{10}$$

A 3 M *n*-butyllithium solution in heptane is added dropwise to 1 M ethereal hydrazoic acid. Lithium azide precipitates immediately and after separation is washed with ether [61].

In another metalorganic reaction, small amounts of lithium azide were made:

$$(C_6H_5)_3SiN_3 + C_6H_5Li \longrightarrow LiN_3 + (C_6H_5)_4Si$$

Ethereal solutions of triphenylsilyl azide and phenyllithium were mixed at room temperature to precipitate LiN_3 in 83% yield [84].

Finally, small quantities of lithium azide have been obtained from lithium amide and nitrous oxide [85]; details are given below under sodium azide (Wislicenus method). The formation of some lithium azide was detected when lithium metal and ammonium azide were reacted in liquid ammonia, but the reaction has not been used for preparation purposes [86].

2. Sodium Azide

Sodium azide, NaN_3, is a white salt which dissolves readily in water (28% w/w at 0°C; 29.5% at 21°C; 34% at 80°C; and 35.5% at 100°C [87]) and less readily in 1,2-ethanediol, 2-methoxyethanol, and formamide. The azide crystallizes from these solvents as the rhombohedral beta form [88]; for other modifications, see Chapter 3. It is practically insoluble in alcohol, ether, acetone, tetrahydrofuran, toluene, chloroform, 2-butanone, methyl acetate, and methyl urethane [88].

Sodium azide is not sensitive to impact or friction. When heated in nitrogen to 365°C, it decomposes without a flame or explosion; in oxygen, the sodium catches fire, and the mass burns in the typical fashion of the metal.

Sodium azide is produced in large quantities commercially, and according to Ribaudo and coworkers [89], the products contain typically the following elemental impurities: Ca, 150 ppm; Mg, 22; Fe, 20; S, 19; Sr, 7; Al, 4; K, 4; Si, 4; Cl, 4; Ni, 2; and Cu, 2. Carbonate and nitrate are normal anion impurities. The commercial grade is sufficiently pure for organic syntheses (after "activation" with hydrazine), but is often required in a purer state for research purposes. Research grades may be made by any of the methods listed for sodium azide in Table V.

The Wislicenus process (see p. 24), for example, may be conducted as follows. Several iron boats containing sodium metal are placed in a horizontal combustion tube and heated in nitrogen to 250-300°C; the gas is then changed to dry ammonia until the molten metal is converted to sodamide. The temperature is then lowered to 170-190°C and the gas changed to nitrous oxide, N_2O, until no more ammonia is detected in the waste gases. The crude product (sodium azide + sodium hydroxide) is leached with water and after filtering concentrated to incipient crystallization. Some azide is retained in the caustic liquid, from which it may be precipitated with alcohol.

Selecting the proper reaction vessel is of concern in this process as many materials are corroded by the molten sodamide and some metals form explosive azides. Nickel [90], aluminum [91], and iron [92] are recommended; platinum is corroded [86].

The liquid ammonia version of this process [15] is described as follows:

> Using a three-necked, two-liter flask provided with stirring mechanism, a curved inlet tube reaching to the bottom of the flask and a vent tube, one liter of anhydrous ammonia was placed in this flask and 0.3 gram of ferric nitrate as catalyst, to which was gradually added 26 grams of metallic sodium. Conversion to sodamide took place immediately. During continued stirring nitrous oxide was bubbled through the solution in the amount of 567 grams over a period of 11 hours. At the completion of the reaction, sufficient methanol was added to destroy any unchanged sodamide. The ammonia was evaporated, the solid taken up with water and the sodium azide separated. The conversion to sodium azide, based on the sodium, was 93.2 percent of the theoretical.

Table V. Preparative Methods for IA Metal Azides

Reactants	Azide products				
	Li	Na	K	Rb	Cs
Metalamide + nitrous oxide (Wislicenus process)	x	x	x	x	x
Metal hydroxide + hydrazine + nitrite (Thiele process)	x	x	x		
Metal + hydrazoic acid	x	x	x	x	x
Metal carbonate + hydrazoic acid	x	x	x	x	x
Cation exchange resin + sodium azide	x				
Metal sulfate + barium azide	x	x	x	x	
Metal chromate + barium azide					x
Metal sulfate + sodium azide	x				
Metal chloride + sodium azide	x				
Metal organyl + trimethylsilyl azide	x				
Metal organyl + hydrazoic acid	x				
Metal + ammonium azide in liquid ammonia	x	x	x		

Levering's invention of the same process as a one-step synthesis at elevated pressure [93] may also be used:

> A 500-ml stainless steel rocking type autoclave was charged with 11.5 g (0.5 mole) of clean dry sodium. The autoclave was capped, sealed, cooled in Dry Ice and evacuated. Liquid ammonia, 100 g (5.9 moles), was weighed in and the bomb placed in a jacket through which a liquid was circulated. The temperature was raised to 45°C and nitrous oxide was added in increments over a period of 2.5 hours maintaining the temperature at 45 to 50°C. All of the gas was removed after 0.5 hour of reaction and found to contain 0.13 mole of hydrogen. Reaction was continued with fresh nitrous oxide. When no further gas absorption occurred the reactor was cooled to 20°C, vented and the product removed. Ninety-eight percent of the sodium was recovered as sodium azide (0.19 mole) and sodium hydroxide (0.302 mole). The conversion to sodium azide was 38 percent. The gas at the end of the reaction contained only a small amount of hydrogen; it was mainly nitrous oxide.

Alternatively, sodium azide may be made by the classical hydrazine oxidation method of Thiele [17] and Stolle [18]:

$$R{-}ONO + H_2N{-}{-}NH_2 + NaOR \longrightarrow NaN_3 + 2ROH + H_2O$$

in which an alkyl nitrite is reacted in organic solvents with hydrazine in the presence of alkali. The resulting sodium azide, as the most insoluble component, precipitates from the mixture. Since its invention in 1908 numerous variations have been published, recommending the use of ethyl nitrite [17,18,94], propyl nitrite [95], butyl nitrite [96], amyl nitrite [18,97] with sodium methylate [95], ethylate [17,18], or hydroxide [96,97] in alcoholic, alcoholic-ethereal, or even aqueous solutions. Depending on the boiling points involved, the reaction temperatures range from -10 to +78°C. As an example, 8.1 g sodium methylate (0.14 mol) is dissolved in 50 ml methanol and cooled to 10°C. Six grams hydrazine hydrate (85% = 0.1 mole) is added, followed by a solution of 15.5 g butyl nitrite (0.15 mol) in 100 ml ether. With occasional stirring the mixture is kept for 1 hr below room temperature. Sodium azide precipitates and, after standing at room temperature overnight, is separated and washed with acetone. With respect to hydrazine the yield of the crude product is 88% (5.7 g).

While the Thiele process is conducted in alkaline media, Hodgkinson [98] obtained a patent for oxidizing hydrazine with nitrite in neutral solution. The produced azide was precipitated as silver azide and the latter in bulk agitated with common salt to form sodium azide and silver chloride.

The above methods involve synthesis of the azide group itself and should only be considered when the commercial sodium azide cannot be sufficiently purified or its preparation from hydrazoic acid is not feasible, as may be the case when isotope-enriched samples (^{15}N) are needed. In the majority of cases, however, sodium azide is best prepared via hydrazoic acid. Purifying the commercial

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salt may also be satisfactory, especially with respect to cations, but foreign anions are difficult to remove. For the same reason it must be considered that the analytical data supplied with commercial chemicals are incomplete, as the suppliers may list, at their discretion, only "those impurities of concern in applications for which each chemical is most commonly used" [99]. Thus, a sodium salt of "ultrapure" grade may list the metal impurities present between 0.01 and 100 ppm, but no anion impurities although present in quantities up to several percent.

Sodium azide may be made by neutralizing sodium hydroxide or carbonate with hydrazoic acid. For example, the vapors from a hydrazoic acid generator (p. 28) may be bubbled into 100 ml of a 25% sodium carbonate solution. At first sodium bicarbonate is precipitated, and when the solution is heated carbon dioxide is driven off. The reaction is completed when all is dissolved and a baryta test indicates absence of carbonate. Then 900 ml alcohol and 200 ml ether are added to precipitate 30 g sodium azide [39]. In another approach, small amounts of pure sodium azide were made by reacting sodium metal with HN_3 in a vacuum line [100].

If barium azide is available, it may be converted to sodium azide by metathesis with sodium sulfate [62,101,102]. The hazards of handling hydrazoic acid are thus avoided, but the product is inherently less pure.

3. Potassium Azide

Potassium azide, KN_3, dissolves readily in water (solubility, 29% w/w at 0°C; 34% at 20°C; 38.4% at 40°C; 47.2% at 80°C; and 51.4% at 100°C [62,87]) from which it grows easily into large, colorless crystals. In alcohol (solubility, in ethanol, 0.14% w/w at 16°C [62]) and acetone it is practically insoluble. The salt melts in evacuated glass tubes at 350°C [103] and in quartz at 343°C [104]. About 10° above melting it decomposes, and once triggered the reaction continues even at lower temperatures. Near 350°C the decomposition proceeds slowly enough to grow crystals from the melt [105]; above 360°C it becomes rapid and has been used for making high-purity nitrogen [103]. In the presence of oxygen the combustion proceeds with sputtering, but the azide is not sensitive to impact or friction.

Commercially, the compound is made from sodium azide by metathesis with potassium salts and separated from the solution on the basis of differential solubilities. Thus sodium azide and potassium carbonate, when mixed in suitable concentrations, yield potassium azide upon cooling [106]:

$$NaN_3 + \tfrac{1}{2}K_2CO_3 \longrightarrow KN_3 + \tfrac{1}{2}Na_2CO_3$$

Similarly, KN_3 may be made on a small scale by mixing aqueous solutions of potassium hydroxide and sodium azide; the potassium azide is precipitated with alcohol [107]. Other laboratory methods include the Wislicenus synthesis from potassium amide which may be conducted in a horizontal iron cylinder, 50 mm

in diam. and 250 mm long. This is fitted with gas vents, charged with 30 g potassium, and heated to 300°C. Ammonia gas is then passed through the rotating cylinder until all metal is converted; nitrous oxide completes the synthesis at 165°C. The melt is eluted from the cooled cylinder with hot water, filtered, and concentrated to incipient crystallization. The yield is 29.6 g (theoretically 31.1 g) [49].

Potassium azide has also been synthesized from hydrazine and alkyl nitrite (Thiele process), by neutralizing hydrazoic acid with potassium hydroxide or carbonate, or by reacting barium azide with potassium sulfate. The reactions are essentially the same as described under sodium azide.

4. Rubidium Azide

Rubidium azide, RbN_3, is slightly hygroscopic [62] and very soluble in water (51.7% at 16°C, 53.3% at 17°C [62]) and slightly soluble in ethanol (0.18% w/w at 16°C). Large, colorless crystals grow easily from the aqueous solution. The salt transforms at 315°C from a tetragonal to a cubic phase which melts at 317°C [108]*; the melting is accompanied with vivid gas evolution, leaving cesium metal and cesium nitride [104]. In the presence of oxygen the decomposing mass catches fire and combusts with sputtering. In a strict sense, RbN_3 is sensitive to mechanical shock, but it takes the impact of a 20-kg weight dropping from 20 cm to deflagrate the sample [109]; this compares roughly to the impact sensitivity of TNT.

The salt is made in essentially the same way as described for sodium azide: synthesis according to Wislicenus [86], neutralizing of hydrazoic acid with rubidium carbonate [75], or reacting of rubidium sulfate and barium azide [62,73,101,109].

5. Cesium Azide

Cesium azide, CsN_3, is a white, deliquescent solid of even higher solubility in water than the rubidium salt: The saturated solution contains 69.2% RbN_3 at 0°C and 75.5% at 16°C [62]; ethanol dissolves only 0.94% (w/w) at 16°C [62]. The salt transforms at 151°C from a tetragonal to a cubic phase, which melts at 326°C with decomposition [108],† leaving, like rubidium azide, a mixture of metal and nitride [103]. CsN_3 is not sensitive to mechanical shock.

Like the other 1A azides, CsN_3 is obtainable through the Wislicenus synthesis [85], by neutralizing hydrazoic acid with cesium hydroxide [110] or carbonate [75], or by reacting cesium sulfate [62,101,102] or chromate [73] with barium azide. On account of its deliquescence and high solubility, some

*Melting at 317°C was determined in the differential scanning calorimeter [108]; older visual observations range from 300 to 340°C [62,103,104].

†Melting at 326°C was determined in the differential scanning calorimeter [108]; older visual observations range from 310 to 326°C [62,103,104].

difficulty is encountered in bringing the aqueous solutions to crystallization. After concentration near crystallization, the viscous liquid is reacidified with hydrazoic acid and evaporated in a vacuum desiccator.

G. AZIDES OF THE IIA METALS

Table VI reveals a marked difference in the character of the chemical bond in beryllium and magnesium azides from the rest of group IIA, and the chemical properties and methods of preparation differ accordingly. Beryllium and magnesium azides are moisture sensitive; the former decomposes hydrolytically to $Be(OH)_2$, and the latter forms basic azides. Hence, they are made in water-free media such as liquid ammonia, anhydrous hydrazine, or organic solvents. They deflagrate only weakly when ignited with a flame and are not sensitive to mechanical shock. The other IIA azides can be made in aqueous media, in which they are soluble; some form hydrates in the solid state, and they have the property of explosion. Beryllium azide is the only member of the group which is polymeric.

1. Beryllium Azide

Beryllium azide, $Be(N_3)_2$, is a polymeric [111] white solid which decomposes hydrolytically [62] but dissolves in tetrahydrofuran. It is insoluble in ether and dichloromethane. In a flame it deflagrates weakly, but it is insensitive to thermal or mechanical shock.

Only small samples of the compound have been made, for example, according to

$$Be(CH_3)_2 + 2HN_3 \longrightarrow Be(N_3)_2 + 2CH_4$$

Table VI. Preparative Methods for the IIA Metal Azides

Reactants	Azide products					
	Be	Mg	Ca	Sr	Ba	Ra
Metalamide + nitrous oxide (Wislicenus process)			×			
Metal hydroxide + hydrazine + nitrite (Thiele process)					×	
Metal + hydrazoic acid			×	×	×	
Metal carbonate + hydrazoic acid			×	×	×	×
Metal hydroxide + hydrazoic acid			×	×	×	
Metal oxide + hydrazoic acid			×	×	×	
Metal + hydrazoic acid			×	×	×	
Metal hydroxide + ammonium azide			×	×	×	
Metal + ammonium azide in liquid ammonia		×	×			
Metal + hydrazine azide		×				
Metal chloride + trimethylsilyl azide	×	×				
Metal organyl + hydrazoic acid	×	×				

Hydrazoic acid in a vacuum line at -180°C was condensed onto beryllium dimethyl and allowed to warm up. After melting, the reaction stopped at -116°C with precipitation of $Be(N_3)_2$ [112]. Also, beryllium chloride was refluxed for six days with trimethylsilyl azide in dichloromethane media to obtain a white precipitate which was not completely free of Cl [111]:

$$BeCl_2 + 2(CH_3)SiN_3 \longrightarrow Be(N_3)_2 + 2(CH_3)_2SiCl$$

An identical experiment in ether media yielded beryllium azide chloride in the form of the etherate, $ClBe(N_3)[(C_2H_5)_2O]_2$ [111].

2. Magnesium Azide

Magnesium azide is a white salt which dissolves readily in water [62] but is insoluble in ether [62], tetrahydrofuran [113], and hydrazine [61]. Aqueous solutions hydrolyze to form a basic azide [113]; exposure to atmospheric moisture leads to magnesium hydroxide [62]. The salt deflagrates weakly when heated in a flame. No sensitivity to mechanical shock has been noted.

Aqueous solutions of magnesium azide have been made by dissolving magnesium in hydrazoic acid or reacting barium azide with magnesium sulfate, but its hydrolytic tendency frustrated efforts to isolate it [62,113]. Preparations in nonaqueous media are likewise unsatisfactory because stable adducts with the polar solvent are formed; moreover, the separation from semiazidized byproducts is difficult. In one approach, small quantities of the azide were made by condensing excess ethereal hydrazoic acid onto a frozen (liquid nitrogen) solution of magnesium diethyl in dioxane/ether. The mixture reacted upon warming according to

$$Mg(C_2H_5)_2 + 2HN_3 \longrightarrow Mg(N_3)_2 + 2C_2H_6$$

After pumping the solvents and excess acid off at room temperature, the white product was considered a solvent-free magnesium diazide [113], but in the absence of analytical data and in light of general experience with azidation of magnesium organyls, its purity is unconfirmed.

Larger quantities of $Mg(N_3)_2$ were more conveniently obtained with bis(cyclopentadienyl)magnesium, which is available commercially, in tetrahydrofuran (THF) solution [61]. The reagent was added dropwise to ethereal hydrazoic acid at -80°C. A white precipitate of the adduct $Mg(N_3)_2 \cdot 2THF$ was obtained which was devolatilized for six days at 100°C and 10^{-4} torr to yield a magnesium diazide of 92% purity. In another approach, magnesium turnings were reacted in anhydrous hydrazine media with hydrazine azide to yield a mixture of magnesium azide hydrazinate (85%) and magnesium hydrazide hydrazinate [61]. Equally incomplete were the reactions of trimethylsilyl azide with magnesium halides, in ether or THF, conducted at 100°C in an autoclave: A mixture of 70% magnesium azide and 30% magnesium iodide azide, both as tetrahydrofuranates, was obtained [111]. Finally, there is evidence of magne-

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sium azide being formed when magnesium is reacted with ammonium azide in liquid amm(ı [74].

3. Calcium Azide

Calcium azide, $Ca(N_3)_2$, is a white deliquescent salt which dissolves in water (27.5% at 0°C, and 31% at 15.2°C [62]) and is practically insoluble in ethanol (0.2% at 16°C [62]), acetone, and ether. It crystallizes from aqueous solutions as a 1.5 hydrate below 23°C, as a 0.5 hydrate between 23 and 42°C, and as the anhydric form above 42°C [114]. The anhydric form is also obtained at room temperature by precipitating concentrated aqueous solutions with alcohol or acetone. $Ca(N_3)_2$ decomposes thermally above 110°C [103]; heating above 160°C leads to explosion [115].

Aqueous solutions of calcium azide are obtained from hydrazoic acid and calcium hydroxide; an excess of the latter is precipitated as carbonate by bubbling in CO_2 [62,116]. The solution is then concentrated, reacidified with hydrazoic acid, and precipitated with alcohol, acetone, or mixtures of these; ether may be added to enhance the yield. Instead of the hydroxide, calcium carbonate [117,118] or oxide [73,119] have been used, but hydroxide yields a purer product [39]. If ammonium azide is available, its aqueous solution may be reacted with excess calcium hydroxide according to

$$Ca(OH)_2 + 2NH_4N_3 \longrightarrow Ca(N_3)_2 + 2H_2O + 2NH_3$$

The ammonia is boiled off and excess Ca^{2+} precipitated with CO_2 [62]. Small amounts of $Ca(N_3)_2$ have also been made with the Wislicenus process [85,120]; the intermediate calcium amide forms at 20–60°C, and the azide at 90–100°C.

4. Strontium Azide

Strontium azide, $Sr(N_3)_2$, a white, hygroscopic salt, dissolves in water (31.4% at 16°C) and is practically insoluble in ethanol (solubility at 16°C, 0.09% [62]) and acetone. The compound decomposes at 140°C [62] and deflagrates when heated above 194°C [85,115]. $Sr(N_3)_2$ is made by the methods described for the calcium salt [62,74,75,116,117,119–122,123]. The Wislicenus process is less advisable here, as $Sr(N_3)_2$ is formed at 140–155°C, which is already within the range of its thermal decomposition.

5. Barium Azide

Barium azide, $Ba(N_3)_2$, is the best known member of the group. It is a white salt which dissolves in water (11.5% at 0°C, 14.98% at 15.7°C, 15.36% at 20°C, 22.73% at 52.1°C, 24.75% at 70°C [62,124]) and is practically insoluble in alcohol (solubility in ethanol, 0.017% at 16°C [62]), acetone, and ether. In contact with its solution, a 1.5 hydrate is stable below 11°C [124], a monohydrate between 11 and 52.5°C, and the anhydric form above 52.5°C [,125]. The existence of a 0.5 hydrate has also been claimed [126] but was proven incorrect by thermogravimetric and solubility analyses [124]. Dry crystals of the two hydrated forms turn opaque on continued exposure to air.

The salt begins to decompose at 160°C, and once triggered the reaction continues as low as 120°C [103]. When heated above 217°C it deflagrates with a green flash [62]. Barium azide is also sensitive to mechanical shock, exploding with 50% probability on impact of a 10-kg weight dropping from 10 cm [109].

All preparation methods for $Ba(N_3)_2$ yield first an aqueous solution, from which the salt is precipitated by evaporation or by adding an organic solvent. In either case, mixtures of the monohydric and anhydric forms are obtained, and much confusion about the properties of $Ba(N_3)_2$ as reported in the literature [62,74,109,115,126–131] may be attributed to the uncertain composition of the products used.

Barium azide may be obtained by any of the methods described for calcium azide. When precipitating the aqueous solution, acetone should be preferred as it yields a coarser product [132] which is less likely to contain impurities. The salt has also been synthesized with hydrazine and nitrite: 3.5 g barium hydroxide and 200 ml aqueous hydrazine (5% w/w) were cooled with ice and 15 g ethyl nitrite added dropwise with stirring. The next day, excess hydroxide was removed with CO_2; the filtrate yielded 8 g barium azide (30% of the theoretical yield) [49]. Small samples of barium azide have also been made according to the Wislicenus process; the intermediate amide formed at 260–290°C and the azide at 140–175°C [85], which is, however, already within the range of thermal decomposition.

Barium azide monohydrate, $Ba(N_3)_2 \cdot H_2O$, is made from slow evaporation of its aqueous solution: 30 g common barium azide in 200 ml water is acidified in a plastic dish (glass causes creeping of crystal crusts) with a few milliliters of hydrazoic acid and exposed in a desiccator to phosphorus pentoxide; no vacuum is applied. After 14 days, the crystal mass is washed with water and dried between filter paper. Within a day the dry crystals turn opaque when exposed to air [124]. Anhydrous barium azide, $Ba(N_3)_2$, is made by grinding the common product to a fine powder and exposing it for 24 hr to phosphorus pentoxide at a vacuum of 0.3 torr [133]. Common barium azide, 36 g, may also be dissolved in 100 ml water at 95°C, and the temperature is gradually lowered to 55°C. (If this is done at a rate of 5°C a day or less, the salt separates in the form of large single crystals.) At 55°C the salt is quickly removed from the solution and dried between filter paper. Washing with water starts hydration [124].

6. Radium Azide

$Ra(N_3)_2$ was prepared only once by Ebler in 1910 as a white, crystalline salt, containing barium bromide; it decomposed *in vacuo* between 180 and 250°C

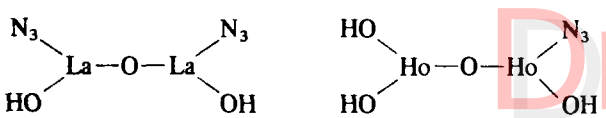
to yield th etal. In the presence of moisture, however, the decomposition proceeded with sputtering and the residue was mainly nitride.

The salt was made from barium-radium bromide which was first enriched by fractional crystallization. Its aqueous solution was then precipitated with ammonium carbonate, and the radium carbonate dissolved in hydrazoic acid. The azide was crystallized at room temperature over sulfuric acid [134].

H. AZIDES OF THE IIIB TO VIIB METALS

1. Basic Azides of Yttrium, Some Lanthanides, and Azido Complexes of Uranium

Normal azides are not known in group IIIB. Curtius and Darapsky [135] attempted to make them by dissolving for example, lanthanum hydroxide in hydrazoic acid. The solution was assumed to contain the normal azide but only basic products were precipitated upon evaporation or by adding alcohol. The precipitate was insoluble in water, had the approximate composition $La(OH)(N_3)_2 \cdot 1.5H_2O$, and deflagrated upon heating. The same results were found with yttrium, cerium, dysprosium, thorium, and uranium azides. Based on the infrared spectra, Rosenwasser and Bryant [136] suggested two types of basic rare earth azides. The lanthanum type (a) was found for lanthanum, neodymium,



(a)

(b)

samarium, europium, gadolinium, and dysprosium; and the holmium type (b) for holmium, erbium, ytterbium, and yttrium.

The uranyl ion, $(UO_2)^{2+}$, forms yellow azido complexes that are stable in dilute (0.01 M) aqueous solutions in the presence of excess azide; a cation structure $[(UO_2)(N_3)]^+$ has been established and was used in the analysis of uranium [137,138]. The anion tetraazido complex has been isolated as the tetraphenylarsonium salt, $[As(Ph)_4]_2[(UO_2)(N_3)_4]$, by admixing a solution of 1 g uranyl nitrate in 2 N nitric acid in nitrogen environment to a solution of 7 g sodium azide. At 80°C the red solution was precipitated with tetraphenylarsonium chloride to obtain yellow crystallites that decomposed at 171°C [139].

2. Titanium Azide Chloride

The only known azide in the group IVB is titanium(IV) azide trichloride, $Ti(N_3)Cl_3$. As a typical mixed azide, the yellow, covalent compound is hygroscopic and moisture sensitive and dissolves only sparingly in c nic solvents. The solid decomposes at 168°C; rapid heating and mechanical shock cause explosion [140]. It was made according to

$$TiCl_4 + ClN_3 \longrightarrow Ti(N_3)Cl_3 + Cl_2$$

with the exclusion of moisture from the reaction and its product, by bubbling a mixture of nitrogen/chlorine azide vapors (for preparation, see under chlorine azide) into the tetrachloride. The gas-inlet tube had a large diameter and was submerged no deeper than 5 mm to avoid pressure fluctuations, which from experience are known to cause the chlorine azide to explode. The solid product was washed with CCl_4 [140].

3. Azides of Vanadium

Several mixed and hetero azides of vanadium(V) as well as azido complexes of vanadium(II) and (V) have been described. The crystalline vanadyl azide trichloride, $VO(N_3)Cl_3$, is made from $VOCl_3$ and chlorine azide as described under the titanium azide. The moisture-sensitive compound deflagrates on thermal shock; it is soluble in $VOCl_3$. The brown, solid vanadium azide tetrachloride, $V(N_3)Cl_4$, was made accordingly from solid VCl_4 and chlorine azide in CCl_4 media. In the dry state at room temperature it is stable for several days, but decomposes with water and, less rapidly, with organic solvents. The compound is very sensitive to friction and impact and also explodes on thermal shock [141].

No explosive properties are reported for the salts of anionic vanadium azido complexes with large organic cations. The hexaazidovanadate(III), $[V^{III}(N_3)_6]^{3-}$, for example, is moisture and oxygen sensitive and is made from VCl_3 and excess sodium azide, and then precipitated as the tetrabutylammonium salt. The pink crystals decompose during recrystallization [142]. Similarly, a green tetraazidovanadylate(IV), $[V^{IV}O(N_3)_4]^{2-}$, is made from $VOCl_2$ in acidic media and isolated with large cations [139,142].

4. Azides of Chromium

Chromium(III) forms the normal azide, a number of basic azides and azido complexes, and a chromium(VI) hetero azide. All these compounds reflect the properties of their respective classes (see p. 21).

Chromium(III) azide, $Cr(N_3)_3$, is a dark green, moisture-sensitive, very hygroscopic solid; its chemical bond is 39% ionic. In water it decomposes to basic products, but dissolves unchanged in alcohol. The compound explodes when shocked thermally or mechanically; basic products deflagrate. Various approaches to make $Cr(N_3)_3$ failed. For example, chromium hydroxide was dissolved in hydrazoic acid, but attempts to isolate it yielded basic products [135]. The same reaction in nonaqueous media likewise failed as ethereal

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hydrazoic acid did not react, and the alcoholic acid again yielded basic azides [54,143]. The compound was finally made by reacting chromium nitrate in a water-free ethanolic solution with solid sodium azide [144]. Basic azides which are more or less water soluble are obtained as hydrolysis products of $Cr(N_3)_3$ [54,135,143] and give analyses between $Cr(OH)_2$ and $Cr(N_3)_3$, without indication of stable stoichiometric phases.

All phases of coordination chemistry are encompassed by the complex chromium(III) azides. A yellow, crystalline salt of the composition $[Cr^{III}(NH_3)_6]^{3-}(N_3)_3$, for example, is not a true azido complex but the azide salt of the hexamminechromium(III) cation. It is soluble in water; the heated solution aquates over a red intermediate, aquopentamminechromium, to chromium hydroxide. The dry salt explodes in the match test. Similarly explosive is the neutral complex triamminetriazidochromium(III), $[(NH_3)_3Cr^{III}(N_3)_3]^0$, an olive-green, crystalline solid which is, expectedly, insoluble in water and organic solvents; it explodes thermally within 25 sec at 250°, and within 1 sec at 300°C, and also on impact [145]. The compound was made by heating a solution of 10 g hexamminechromium perchlorate, 10 g ammonium sulfate, and 50 g sodium azide in 300 ml water for 90 min.

An anion complex, the hexaazidochromate(III), $[Cr^{III}(N_3)_6]^{3-}$, was isolated as the violet crystalline tetrabutylammonium salt. The complex is acetone soluble and decomposes at 255°C; as with other azido complexes with large organic cations, no impact sensitivity was noted. To make it, chromium chloride hexahydrate was digested in 1 N sulfuric acid for 1 hr with excess dry sodium azide and then precipitated with a tetrabutylammonium salt [139].

Chromyl azide, $CrO_2(N_3)_2$, has the properties of a typical hetero azide. The deep violet solid is light and moisture sensitive and decomposes above -100°C. Above -60°C the compound tends to explode spontaneously, but solutions in inert solvents, such as carbon tetrachloride or freon, are stable up to -50°C [58,146]. It was made according to

$$CrO_3 + 2HN_3 \longrightarrow CrO_2(N_3)_2 + H_2O$$

in a vacuum line at -80°C from a mixture of CrO_3 and phosphorus pentoxide, and hydrazoic acid vapors.

Table VII. Force Constants of Metal-to-Azide Bonds in Some Mixed Azides [147]

	Force constant (mdyn/A)
$TiCl_3N_3$	2.95
$VOCl_2N_3$	2.95
CrO_2ClN_3	2.32

Remarkably more stable is the corresponding azide chloride, $(Cr^{VI}O_2)Cl(N_3)$, which is made from chromyl chloride and chlorine azide as described for titanium azide (p. 43). The dark green, amorphous solid is soluble in organic solvents. It decomposes at 150°C and is not sensitive to impact or heat shock [147]. The marked stability of $CrO_2Cl(N_3)$ differs from that of other mixed azides such as $TiCl_3(N_3)$ and $VOCl_2(N_3)$ and is an exception to the rule that covalent metal-to-azide bonds are not stabilized in the presence of halogen ligands at the same atom (p. 21). Analysis of the infrared spectra indicates, however [147], a partly ionic Cr-to-N_3 bond in CrO_2ClN_3, corresponding with a lower force constant (Table VII).

5. Molybdenum Azide Tetrachloride

The only known azide of molybdenum is the black, crystalline $Mo^{V}Cl_4(N_3)$. The compound dissolves sparingly in benzene, decomposes slowly at 80°C, and explodes on thermal shock, friction, and impact. It was made from $MoCl_5$ and ClN_3 in carbon tetrachloride media [147].

6. Azides of Manganese

Of the five oxidation states of manganese, only Mn(II) forms azides. The normal azide, $Mn(N_3)_2$, consists of white, sandy crystals which are chemically and explosively not very stable; thus, exposure to the atmosphere causes a brown discoloration (oxidation to MnO_2), and the compound explodes above 218°C and is sensitive to impact and friction [54,115,143]. The azide is not easy to make, as dissolving manganous carbonate in hydrazoic acid yields basic products [62,135]. Reaction of the dry carbonate with ethereal hydrazoic acid is impractically slow, but the latter yields $Mn(N_3)_2$ when shaken with basic manganese azide for three days [54].

Basic manganese azide, that is to say a white to brownish solid of the approximate composition $(OH)Mn(N_3)$, is obtained from aqueous solutions by precipitation with alcohol [135]. The solid explodes in a flame but is not sensitive to mechanical shock.

Equally sensitive to oxidation is the complex tetraazidomanganate(II), $[Mn^{II}(N_3)_4]^{2-}$. The alkali metal salts are known as monohydrates in the form of large, colorless crystals; like the normal azide, they explode in a flame and on impact and friction [148]. Storage is not feasible as loss of water of crystallization and discoloration (oxidation to MnO_2) are unavoidable. Salts of the complex with large organic cations [139,142] are not impact sensitive. The complex is made in aqueous media from a noncomplexing manganese salt and excess azide; the cesium salt, for example, is made by mixing 10 ml 4 M cesium azide with 10 ml 0.5 M manganese perchlorate at 30°C. Upon cooling, large crystals grow from the brownish solution [148,149].

I. AZIDES OF GROUP VIII METALS

1. Azides of Iron(II)

The normal iron(II) azide has never been isolated. It is supposedly formed when iron(II) salts and sodium azide are mixed, but the colorless solution turns deep red on exposure to the atmosphere, indicating the presence of iron(III) azide [1,62]. Quite stable, in contrast, are two azide halides of the type $XFe^{II}(N_3)$ which have been made by azidation of ironpentacarbonyl with ClN_3 or BrN_3 and subsequent pyrolysis *in vacuo* [150]:

$$Fe(CO)_5 + ClN_3 \longrightarrow Fe(CO)_2(N_3)Cl + 3CO$$

$$Fe(CO)_2(N_3)Cl \longrightarrow Fe(N_3)Cl + 2CO$$

Both compounds are hygroscopic, water-soluble solids and have in contrast to other azide halides no explosive properties. $FeCl(N_3)$ is light gray and $FeBr(N_3)$ brown. The striking stability has been investigated by Lange and Dehnicke [150] with infrared and magnetic analysis and is evidently due to polymerization which employs in this case, both α-N and Cl bridging, leading to the structure:

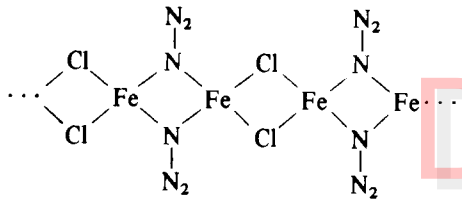

TABLE VIII. Azides of the VIII Metals

	Normal azide	Mixed azide	Azido complex	Metal-organic azide
Iron(II)		x		
Iron(III)	x	x	x	x
Cobalt(II)	x	x	x	x
Nickel(II)	x	x	x	x
Ruthenium(III)			x	
Rhodium(I)			x	
Rhodium(III)			x	
Palladium(II)	x		x	x
Iridium(III)			x	
Platinum(II)			x	x
Platinum(IV)			x	

2. Azides of Iron(III)

The complex hexaazidoferrate(III), $[Fe^{III}(N_3)_6]^{3-}$, forms stable salts with large organic cations. These compounds are soluble in polar organic solvents, such as acetone, nitrobenzene, dimethylformamide, and pyridine; contact with water aquates the complex. Isolated were the tris-(trimethylbenzylammonium) salt, MP 107°C, the tris-(*p*-nitrobenzylpyridinium) salt, MP 112°C; and the sodium bis-(tetramethylammonium) salt, MP 270°C with deflagration [155].

$$Fe_2(SO_4)_3 + 6NaN_3 \longrightarrow 2Fe(N_3)_3 + 3Na_2SO_4$$

Dry, finely ground iron(III) sulfate is suspended in absolute methanol and agitated with dry sodium azide. The solution turns deep red; it is decanted and evaporated *in vacuo* to yield black-brown, leafy crystals of $Fe(N_3)_3$ [54]. Reactions in aqueous media, e.g., dissolving iron metal in hydrazoic acid [153] or treating iron(III) salts with sodium azide [135], lead upon concentration to poorly defined basic products.

Formation of iron(III) azide was also observed by electrolyzing a solution of ammonium azide in liquid ammonia with an iron anode. The characteristic red color appeared near the anode, but no product was isolated [154].

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3. Azides of Cobalt

The normal cobalt(II) azide, $Co(N_3)_2 \cdot xH_2O$, is a reddish-brown, hygroscopic solid which dissolves readily in water; the solution hydrolyzes slowly. It explodes with high brisance when shocked thermally or mechanically. Its sensitivity is considered the highest of all metal azides [54,143].

It was made by dissolving finely ground cobalt carbonate in ethereal hydrazoic acid. After 3–4 days the clear solution is evaporated to obtain reddish-brown crystals. The product, which retains some water tenaciously, is best stored protected from light under ethereal hydrazoic acid [156]. In another approach, cobalt carbonate was dissolved in aqueous hydrazoic acid and the solution concentrated to obtain a basic azide. This was again dissolved in strong hydrazoic acid to produce the reddish-brown crystals. The product was considered to be $Co(N_3)_2$ [157] but was not analyzed.

A basic product of the approximate composition $(OH)Co(N_3)$ is made by heating an aqueous cobalt azide solution to precipitate a violet solid. Dipositive cobalt forms a tetraazidocobaltate(II) complex, $[Co^{II}(N_3)_4]^{2-}$, in aqueous cobalt(II) salt solutions with a 15-fold sodium azide excess at pH 5 and may be

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isolated with large organic cations (Table IX). These compounds have sharp melting points, dissolve in acetone and chloroform, and do not explode [158,159].

4. Azides of Nickel

The normal azide, $Ni(N_3)_2$, is a green, hygroscopic solid which dissolves readily in water; upon standing or heating, hydrolyzed products are precipitated [135]. The compound is extremely sensitive to thermal or mechanical shock [54].

Two methods of preparation are known: Nickel hydroxide is dissolved in an excess of strong hydrazoic acid; to the green solution, alcohol and ether are added to precipitate the azide as a light green, sandy powder [135]. Or, a suspension of nickel carbonate in ethereal hydrazoic acid may be allowed to stand at room temperature for 3–4 days until the suspension is dissolved [54].

Upon standing, aqueous solutions of nickel azide separate as green flakes which appear to be mixtures of the normal $Ni(N_3)_2$ and the basic $(HO)Ni(N_3)$ [62]. The pure basic nickel azide has been established by X-ray studies [160], but its preparation was not described.

Potassium hexaazidonickelate(II), $K_4[Ni(N_3)_6]^{4-}$, is a yellow-green solid which dissolves to some degree in water and is insoluble in alcohol. The salt deflagrates in a flame test but is not sensitive to mechanical shock [161]. It was obtained by mixing solutions of nickel azide and a tenfold excess potassium azide. A solution of nickel azide was first made by dissolving basic nickel carbonate in hydrazoic acid. The green solution, which was 0.2 M with respect to Ni, was then poured into the potassium azide solution (concentration, 25 g KN_3 in 100 ml water). Within a week the complex salt separated as a mass of fine crystals that were washed with ice-cold water and alcohol [161].

5. Azides of Ruthenium

Ruthenium forms several mixed azido complexes and one all-azido complex. The crystalline solids and their solutions are light sensitive. The tetraethylammonium salt, $[(C_2H_5)_4N]_3[Ru^{III}(N_3)_6]$, is made by adding 0.2 g $K_2[Ru^{IV}Cl_6]$ to a 40°C solution of 13 g sodium azide in 40 ml water and 20 ml ethanol. Ru(IV) is reduced to Ru(III) and nitrogen evolves. When the color changes from orange to red and the gas evolution ceases, an aqueous solution of 4 g tetraethylammonium bromide is added and the solution is concentrated to yield brick-red crystals of the above complex salt [162].

6. Azides of Rhodium

All azide compounds of this element are complexes, namely, several mixed azide bridged complexes of Rh(I) [163], several mixed azido complexes of Rh(III) [164,165], and a hexaazidorhodate(III).

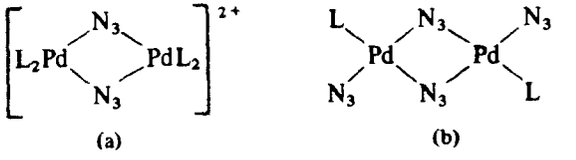
The complex anion hexaazidorhodate(III), $[Rh^{III}(N_3)_6]^{3-}$ (nown as tetraphenylarsonium salt [139] and as tetrabutylammonium salt [162]. For preparation of the former, see Table IX. The tetrabutylammonium hexaazidorhodate(III) is obtained from the $[RhCl_6]^{3-}$ complex by ligand exchange: 0.2 g $Na_3RhCl_6 \cdot 12H_2O$ is dissolved in 25 ml water and added to a solution of 1.5 g sodium azide in 50 ml water. The mixture is kept at 40°C for 1 hr and then precipitated with 1 g tetrabutylammonium bromide. The faintly red crystals are washed with alcohol and, from a methylene chloride solution, reprecipitated with ether [162].

7. Azides of Palladium

Not much is known about the normal azide $Pd(N_3)_2$ except that it is a brown, water-insoluble solid which is very sensitive to heat, friction, and impact [139,158]. It is precipitated when solutions of palladium salts and azide are combined, e.g., 0.1 M sodium azide and 0.01 M palladium perchlorate are mixed in molar ratios, but the precipitate cannot be dried without exploding [166]. This azide is occasionally obtained as an undesired intermediate to the complex palladium azides.

Complex palladium azides are obtained by dissolving palladium salts in excess azide, e.g., palladium nitrate and sodium azide (1:4) yield a triazido anion, $[Pd^{II}(N_3)_3]^-$ [167]. Similarly, a tetraazido anion, $[Pd^{II}(N_3)_4]^{2-}$, is obtained from $K_2[PdCl_4]$ by ligand exchange [162]. Another all-azido anion is the azide-bridged, binuclear complex $[Pd_2(N_3)_6]^{2-}$ [168]. All of these have been isolated as salts of large organic cations.

Also known are a variety of mixed azido complexes such as the neutral structure $[L_2Pd^{II}(N_3)_2]^0$ [168,170] and its binuclear variation, $[LPd^{II}(N_3)_2]_2^0$ [168]. A binuclear cation of the suggested composition (a) [171] and a neutral



(a) (b)

binuclear structure (b) [172] have also been reported. The ligand L in the above formulas stands for large neutral ligands such as triphenylphosphine, 1,2-vinylenebis(diphenylphosphine), *N*-dimethylphenylbiguanide, etc. To make the cetyltrimethylammonium tetraazidopalladate(II), $[(C_{16}H_{33})(CH_3)_3]_2[Pd^{II}(N_3)_4]$, for example, 0.1 g potassium tetrachloropalladate(II), $K_2[PdCl_4]$, and 1.6 g sodium azide are dissolved in 10 ml water and heated to 40°C for 10 min. An aqueous solution of cetyltrimethylammonium bromide is then added in excess to precipitate the yellow solid. The compound deteriorates after several days [162].

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Table IX. Synopsis of Complexation Methods

Complex	Media[a]	Reactant for: Central atom	Reactant for: Azide ligand (molar excess)	Reactant for: Cation	Remarks
$[UO_2(N_3)_4]^{2-}$	1, 4, 6	$UO_2(NO_3)_2$	NaN_3 (50)	LC[b]	
$[V^{III}(N_3)_6]^{3-}$	1, 3	VCl_3	NaN_3 (10)	LC	Sensitive to oxidation
$[V^{IV}O(N_3)_4]^{2-}$	1, 3, 6	$VOCl_2$	NaN_3 (30)	LC	
$[Cr^{III}(N_3)_6]^{3-}$	1, 4, 5	$CrCl_3$	NaN_3 (80)	LC	
$[(NH_3)_3Cr^{III}(N_3)_3]^0$	1, 4	$[(NH_3)_6Cr]^{3+}$	NaN_3 (10)		
$[Mn^{II}(N_3)_4]^{2-}$	1, 3	$Mn(ClO_4)_2$	N_3^-(8)	1A metal	
$[Fe^{III}(N_3)_6]^{3-}$	1, 3	$FeCl_3$	NaN_3 (80)	LC	Sensitive to moisture
$[Co^{II}(N_3)_4]^{2-}$	1, 3, 5	$Co(ClO_4)_2$	NaN_3 (40)	LC	
$[Ni^{II}(N_3)_6]^{4-}$	1, 3	$Ni(N_3)_2$	KN_3 (10)	K^+	
$[Ru^{III}(N_3)_6]^{3-}$	1, 2, 4	$K_2Ru^{IV}Cl_6$	NaN_3 (400)	LC	Complexation involves redox reaction; sensitive to light
$[Rh^{III}(N_3)_6]^{3-}$	1, 3, 5	$Rh(NO_3)_3$	NaN_3 (90)	LC	
$[Pd^{II}(N_3)_4]^{2-}$	1, 3, 5	$Pd(NO_3)_2$	NaN_3 (50)	LC	
$[Ir^{III}(N_3)_6]^{3-}$	1, 2, 4	Na_3IrCl_6	NaN_3 (400)	LC	
$[Pt^{II}(N_3)_4]^{2-}$	1, 4	K_2PtCl_4	NaN_3 (100)	LC	Decomposition within hours
$[Pt^{IV}(N_3)_6]^{2-}$	1, 4	K_2PtCl_6	NaN_3 (200)	LC	
$[Cu^{I}(N_3)_2]^-$	1, 3	Cu^{2+}, hydrazine	NaN_3 (80)	LC	Sensitive to oxidation
$[Cu^{II}(N_3)_3]^-$	1, 3	$Cu(ClO_4)_2$	NaN_3 (200)	LC	
$[Cu^{II}(N_3)_6]^{4-}$	2, 4	$Cu(ClO_4)_2$	N_3^-(50)	Li^+, Ba^{2+}	
$[A_2Cu^{II}(N_3)_2]^0$	2, 4	A[c] + $Cu(ClO_4)_2$	NaN_3 (50)		
$[Au^{I}(N_3)_2]^-$	Dichloromethane, 3	AuCl	NaN_3 (25)	LC	Sensitive to light
$[Au^{III}(N_3)_4]^-$	1, 3	$KAuCl_4$	NaN_3 (40)	LC	Decomposition within days
$[Zn^{II}(N_3)_4]^{2-}$	1, 3	$Zn(ClO_4)_2$	NaN_3 (25)	LC	
		$ZnCO_3$	HN_3	IA metal	
$[Cd(py)_2(N_3)_2]^0$	1, 3	$Cd(ClO_4)_2$	py + NaN_3 (20)		
$[Hg^{II}(N_3)_3]^-$	1, 3, 5	$Hg(ClO_4)_2$	NaN_3 (100)	LC	
$[B(N_3)_4]^-$	Ether, low temp.	$LiBH_4$	HN_3	Li^+	Sensitive to moisture
$[Al(N_3)_4]^-$	Benzene, THF, 3	$AlCl_3$	NaN_3 (20)	Na^+	Sensitive to moisture
$[C(N_3)_3]^+$	Boiling CCl_4	$SbCl_4(N_3)$			
$[Sn^{IV}(N_3)_6]^{2-}$	1, 3, 5	$(NH_4)_2SnCl_6$	NaN_3 (100)	LC	
$[Pb^{IV}(N_3)_6]^{2-}$	Dichloromethane, 1, 3	$(NH_4)_2PbCl_6$	NaN_3 (150)	LC	Sensitive to light
$[P^{V}(N_3)_4]^+$	Nitrobenzene, 3	$[M_3PCl]SbCl_6$	NaN_3		
$[As^{V}(N_3)_4]^+$	Nitrobenzene, 3	$[M_3AsCl]SbCl_6$	NaN_3		
$[Sb^{V}(N_3)_4]^+$	Nitrobenzene, 3	$[M_3SbCl]SbCl_6$	NaN_3		

[a] 1 = water; 2 = alcohol; 3 = room temperature; 4 = 40–60°C; 5 = $p_H < 5$; 6 = $p_H < 3$.
[b] LC = large organic cation; e.g. tetra-alkylammonium, tetraphenylarsonium.
[c] A = organic base; e.g., quinoline.

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8. Azides of Iridium

Iridium(III) forms several mixed azido complexes and the hexaazidoiridate anion, $[Ir^{III}(N_3)_6]^{3-}$. The latter is known as the tetrabutylammonium salt [162]. For preparation, see Table IX.

9. Azides of Platinum

A normal platinum azide is not known, but complex azides of both Pt(II) and Pt(IV) have been described. When investigating the latter, Curtius and Rissom [62] obtained red solutions of the potassium salt which exploded violently when heated, and a dark red residue, obtained upon concentration, exploded spontaneously with high brisance. The sensitivity disappears in combination with large organic cations or amine ligands, yielding compounds that decompose slowly when heated but are stable to impact. They are, however, photosensitive and will deteriorate within hours or days.

The tetraazidoplatinate(II), $[Pt^{II}(N_3)_4]^{2-}$, is formed when 0.1 g K_2PtCl_4 and 1.6 g sodium azide are heated in 10ml water for 10 min to 40°C; it is precipitated with large cations as orange salts [139,162,173]. The corresponding complex of tetrapositive platinum, $[Pt^{IV}(N_3)_6]^{2-}$, is prepared from H_2PtCl_6 in the same manner [139,173,174].

Also known are some neutral azido complexes of Pt(II) containing large amine or phosphine ligands (L), such as $[LPt^{II}(N_3)_2]^0$ [169], and $[L_2Pt^{II}(N_3)_2]^0$ [169,172].

J. AZIDES OF THE IB AND IIB METALS

The normal azides of this group are powerful explosives, displaying various degrees of sensitivity, and two of them are of prime interest in explosives technology: silver azide as an initiator for explosive devices, and copper azide as

Table X. Azides of the IB and IIB Metals

	Ionic character of the azide bond (%)	Normal azide	Mixed azide	Hetero azide	Azido complex	Metal-organic azide
IB						
Cu	26	×	×		×	×
Ag	26	×		×	×	
Au	9				×	
IIB						
Zn	39	×	×		×	×
Cd	34	×			×	×
Hg	26	×			×	

an unintentional, treacherous contaminant. Gold azide has the highest sensitivity of any normal metal azide and has not yet been investigated. Copper(II) and mercury(II) azides are exceptions to the traditional pseudohalide rule as they are, unlike the halides, insoluble in water. (See Table X.)

1. Azides of Copper

Over 30 publications deal with the chemistry of copper azides, describing a large variety of explosive solids with colors ranging from blue-violet to blue, blue-green, moss green, yellow-green, yellow, yellow-brown, red, black, gray, and white. Originally only four compounds were believed to exist, namely, a red $Cu^I(N_3)$, a black-brown $Cu^{II}(N_3)_2$, a yellow hydrated $(HO)Cu(N_3)$, and a blue "double salt" (azido complex) with pyridine. Later investigations revealed a far more complicated picture. It was found that side reactions, such as photolysis, hydrolysis, and [in the case of Cu(I)] oxidation, lead to a wealth of mixed phases. Also, a large number of complex copper azides were prepared, mainly by Cirulis and Straumanis; these include the azide salts of complex cations, such as $[Cu^{II}(NH_3)_4]^{2+}$, anion structures including $[Cu^{II}(N_3)_6]^{4-}$, $[Cu^{II}(N_3)_4]^{2-}$, $[Cu^{II}(N_3)_3]^-$, and the azide-bridged $[(N_3)_2Cu^{II}(N_3)Cu^{II}(N_3)_2]^-$. The same authors were able to untangle much of the conflicting earlier findings. Recent studies with physical methods have verified the stoichiometric phases which are individually described below.

All copper azides explode, but the sensitivities vary widely. It is extremely high in the normal azides, $Cu(N_3)$ and $Cu(N_3)_2$. At the other end of the scale are almost insensitive azido complexes of large organic cations. In general, a copper azide is more sensitive than the respective lead azide.

Copper azides are formed with relative ease when copper or brass are in contact with moist hydrazoic acid vapors or solid metal azides. This behavior creates a particular safety hazard, and hardware containing copper or brass cannot be tolerated in the vicinity where azides are prepared or stored. Further details are discussed in Chapter 3, Volume 2.

Cu(I) azides are photosensitive, and both the Cu(I) and azide groups appear to react independently. In addition, Cu^+ is oxidized when exposed to atmospheric oxygen. The normal Cu(I) azide, $Cu(N_3)$, is a white, crystalline solid. On account of its reactivity, however, it is usually obtained as a gray-green powder [175]. Exposure to light leads soon to a dark red product [1] while nitrogen is evolved [175]. The compound is insoluble in water and organic solvents. It is extremely sensitive to heat (temperature of explosion, 220°C [176], impact, and friction.

The compound is made by agitating a Cu(I) salt with sodium azide in the presence of a reducing agent, e.g., a concentrated solution of copper(II) sulfate is reduced with potassium sulfite. The precipitated copper(I) sulfite is dissolved by adding acetic acid, followed by adding sodium azide to precipitate the CuN_3 as a light gray-green powder. After washing with alcohol and ether, the product

is dried *in vacuo* [175-177]. Copper(II) hydroxide may also be reduced with hydrazine, and the acidified solution is treated with sodium azide as above [178]. CuN_3 is also obtained by suspending 5 g copper(I) chloride in a saturated sodium chloride solution. After adding 2 ml of a 3% bisulfite solution, the acidified mixture is treated with sodium azide [179,180].

White, powdery CuN_3 is obtained as an intermediate when copper metal is allowed to stand under hydrazoic acid for several days. Further exposure leads, after some weeks, to $Cu(N_3)_2$. CuN_3 is further obtained by reduction of copper(II) azide:

$$Cu(N_3)_2 \longrightarrow Cu(N_3) + 3N$$

The reduction takes place in aqueous media by gentle heating with hydrazine or in alcohol by heating with hydroxylamine [181].

The complex anion diazidocuprate(I), $[Cu^I(N_3)_2]^-$, is isolated as the tetraphenylphosphonium salt by dissolving CuN_3 (preparation, see above) in hydrazoic acid; upon adding tetraphenylphosphonium chloride, the white salt is precipitated. The compound oxidizes readily [139].

Ethanolic solutions of 5 g triphenylphosphine and 1 g cupric chloride are combined to reduce the Cu^{2+} and precipitate a white substance which is washed and dried. In a nitrogen atmosphere the substance is then dissolved in dichloromethane and shaken with dry sodium azide. From the filtrate, a complex $[(N_3)Cu^IL_2]^0$ (L = triphenylphosphine), is precipitated with hexane [164,182].

Normal copper(II) azide, $Cu(N_3)_2$, is a nonvolatile, crystalline solid of a black to black-brown color which is insoluble in water and organic solvents. It dissolves readily in the presence of excess azide ions, the brown solution containing azido cuprates(II) of varying compositions. Copper(II) azide undergoes some surface hydrolysis when prepared in aqueous media; these products often have a yellow tinge. In boiling water, the solid eventually hydrolyzes to black CuO. Copper(II) azide is not reported to be light sensitive, but the compound is extremely sensitive to thermal and mechanical shock (temperature of explosion, 202°). It explodes on friction or impact with high brisance, even under water [62], and slow decomposition may accelerate into explosion [2].

To form copper(II) azide from copper metal, finely divided copper is left in contact with dilute hydrazoic azid (2%) for approximately two months. After a few days, white Cu(I) azide begins to appear as an intermediate. The presence of oxygen or other oxidants (e.g., hydrogen peroxide) is essential to obtain Cu(II) azide quantitatively as black-violet microcyrstals [62,181,183].

Similarly, copper(II) azide has been made by exposing finely divided CuO for several days to hydrazoic acid [178].

To prepare copper(II) azide from sodium azide and copper(II) salt in aqueous media, solutions of 5 g copper(II) nitrate in 200 ml water, and of 2.5 g sodium azide in 50 ml water are mixed. Copper(II) azide is precipitated in the form of dark brown microcrystals which are washed with water. The product is contaminated with a hydrolyzed surface layer which is removed by adding 2%

hydrazoic acid and letting it stand for one day. After washing with alcohol and ether, the pure product is then dried *in vacuo* [181].

Hydrolysis is avoided in nonaqueous media, when ethanolic solutions of copper(II) nitrate (water free) and lithium azide are mixed to precipitate the black-brown copper(II) azide [181]. Likewise, stoichiometric volumes of sodium azide and copper(II) perchlorate, in acetone containing 10% (v/v) water, may be added slowly to a large volume of acetone. A red precipitate of acetone-solvated copper(II) azide is obtained, which after washing is dried at 110°C to obtain the free azide (color change to brown) [184]. Similarly, the azide has been precipitated by mixing alcoholic solutions of hydrazoic acid and copper acetate [185].

Basic copper(II) azides occur as four distinct phases (Table XI), which have been described as water-insoluble, explosive solids. They are less sensitive to thermal and mechanical shock than the normal azide: the $Cu(N_3)_2 \cdot Cu(OH)_2$ phase explodes at 245°C (normal azide, 202°C) and deflagrates on impact. In principle these compounds are formed by partial hydrolysis of $Cu(N_3)_2$, or by partial azidation of $Cu(OH)_2$:

$$Cu(N_3)_2 + H_2O \longrightarrow (OH)Cu(N_3) + HN_3$$

$$Cu(OH)_2 + HN_3 \longrightarrow (OH)Cu(N_3) + H_2O$$

In accordance with the former reaction, $Cu(N_3)_2 \cdot Cu(OH)_2$ may be prepared when a distilling flask with gas inlet tube is charged with 100 ml water and 1 g copper(II) azide. The receiver contains 50 ml water to which is added 67 ml of a 0.1 N barium hydroxide, and phenolphthalein as an indicator. At 70–80°C a stream of air is bubbled through, carrying hydrazoic acid vapors into the receiver. The operation is interrupted at the turn of the indicator (3–5 hr) [176]. The compound is also obtained in accordance with the second reaction from a solution of 2.6 g sodium azide in 100 ml water, to which is added a mixture of 10 g copper sulfate pentahydrate in 150 ml water and 1.6 g sodium hydroxide in 150 ml water [179].

To prepare the basic azide $Cu(N_3)_2 \cdot 2Cu(OH)_2$, a mixture of 12 g copper acetate in 200 ml water and 3.2 g sodium hydroxide in 200 ml water is added to a solution of 2.65 g sodium azide in 100 ml water [179].

Table XI. Basic Copper(II) Azides

	Phase	Color	Reference
Normal azide	$Cu(N_3)_2$	Black	176, 179, 186, 187
Basic azides	$Cu(N_3)_2 \cdot Cu(OH)_2$	Yellow-brown	176, 186, 189
	$Cu(N_3)_2 \cdot 2\,Cu(OH)_2$	Yellow-green	160, 179, 186, 187
	$Cu(N_3)_2 \cdot 3\,Cu(OH)_2$	Green	179, 187
	$Cu(N_3)_2 \cdot 8\,CuO$	Blue-green	187
Hydroxide	$Cu(OH)_2$	Blue	

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Like the compound $Cu(N_3)_2 \cdot 3Cu(OH)_2$ is made when a solution of 16 g copper acetate in 250 ml water and 4.8 g sodium hydroxide in 250 ml water is added to a solution of 2.86 g sodium azide in 100 ml water [179].

Tetramminecopper(II) azide, $[(NH_3)_4Cu^{II}]^{2+}(N_3)_2$, the azide salt of the well-known tetramminecopper cation, is a blue, crystalline solid with explosive properties. It decomposes within a few days by losing two NH_3, to form diazidodiamminecopper (see below). In contact with water the same reaction occurs rapidly. The salt is made either by dissolving the normal copper azide in liquid ammonia and evaporating the blue solution [183], or by exposing $Cu(N_3)_2$ to dry ammonia gas [189].

Diamminediazidocopper(II), $[(NH_3)_2Cu^{II}(N_3)_2]^0$, the primary decomposition product of the above complex, was formerly considered the azide salt of a cationic complex [188], i.e., of the composition $[(NH_3)_2Cu^{II}]^{2+}(N_3)_2$, but its chemical behavior [190] and crystal structure [191] support the constitution of a neutral azido complex. It is a blue, crystalline solid which is insoluble in water. The compound deflagrates on friction or impact. In a flame it explodes violently after apparently first decomposing to $Cu(N_3)_2$, which is suggested by the color change and its temperature of explosion (202°C).

The compound has been prepared in a number of ways [188,190-192]. For example, tetramminecopper(II) sulfate is precipitated in an aqueous solution with sodium azide, or $Cu(N_3)_2$ is dissolved in aqueous ammonia and the deep blue solution concentrated [188]. Approximately 40 related compounds of the composition $[A_2Cu^{II}(N_3)_2]^0$ (A = organic amine) have been made by dissolving copper nitrate and the amine (e.g., isoquinoline) in hot alcohol to which aqueous sodium azide was added. The complexes usually crystallized within a few days [190].

Lithium hexaazidocuprate(II), $Li_4[Cu(N_3)_6]$, may be prepared in accordance with the reaction:

$$Cu(N_3)_2 + 4LiN_3 \longrightarrow Li_4[Cu(N_3)_6]$$

3 g dry copper(II) azide and 4 g dry lithium azide are dissolved in 20 ml boiling ethanol. Upon standing the dark red-brown solution separates a mass of brown crystal needles which are dried at 120°C to yield the brown lithium hexaazidocuprate(II) [193].

Barium tetraazidocuprate(III), $Ba[Cu(N_3)_4]$, may be prepared likewise:

$$Ba(N_3)_2 + Cu(N_3)_2 \longrightarrow Ba[Cu(N_3)_4]$$

To a boiling concentrated solution of barium azide, copper(II) azide is added until saturation. Upon cooling brown crystals of barium tetraazidocuprate(II) dihydrate are separated. The product is washed with ether and dried at 120°C to yield the anhydric compound [193].

Sodium triazidocuprate(II), $Na[Cu(N_3)_3]$, is formed when 10 g copper(II) azide is added to a hot solution of 5 g sodium azide in 20 ml water. After most

of the copper salt has dissolved, the residue is filtered off and 50 ml methanol is added to the hot solution. Upon standing a mass of brown crystals of sodium triazidocuprate(II) dihydrate is separated. After washing with ether the product is dried at 120°C to yield the black-brown anhydric sodium triazidocuprate(II) [193].

When a hot, concentrated solution of rubidium azide is saturated with copper azide and a small excess of rubidium azide is added, upon cooling the rubidium pentaazidodicuprate(II), $Rb[(N_3)_2Cu(N_3)Cu(N_3)_2]$, crystallizes as small crystals. After filtering, the product is washed with cold water and methanol and removed from the filter while moist, to avoid explosion. The product is dried at room temperature to yield the anhydric salt [194].

Salts of the same complex with large organic amines have been made in methanol media by reacting copper nitrate or chloride with the respective amine and sodium azide. For example, to make the methylaniline salt 4.1 g copper nitrate in 30 ml hot methanol is added to 2 g methylaniline in 30 methanol. The blue solution is heated to near boiling, and 4.4 g sodium azide in 10 ml water is added. The red-brown solution is filtered hot to separate brown crystals. Cooling below 40°C is avoided as otherwise sodium nitrate would precipitate. The compound decomposes in water; for other properties see Table XII [195]. Other copper azido complexes with organic bases are prepared like the respective metal salts, also as shown in Table XII.

Table XII. Copper Azido Complexes with Large Organic Cations [131, 190]

Cation	Color	Impact sensitivity	Explosion temperature (°C)
		$[(Cu(N_3)_4]^{2-}$ complex	
Piperdine	Red-brown	Not very sensitive, deflagrates	200 (MP, 125)
Aminocyclohexane	Green	Not very sensitive, deflagrates	Burns (MP, 146)
		$[Cu(N_3)_3]^-$ complex	
Benzylamine	Green	Insensitive	Burns
Piperidine	Brown	Not very sensitive, deflagrates	178
Tetraphenylphosphonium	Olive	Insensitive	Deflagrates 160
		$[(N_3)_2Cu(N_3)_3Cu(N_3)_2]^-$ complex	
Methylaniline	Brown	Not given	203
Dimethylaniline	Red-brown	Not given	174
Ethylaniline	Brown	Explodes	187
Diethylaniline	Brown	Explodes	198
Xylidine	Red-brown	Explodes	185
Pyrrole	Brown	Explodes	155
Quinaldine	Brown	Explodes	190
Methylquinoline	Brown	Explodes	219

2. Silver Azide

Silver azide, AgN_3, is a white crystalline solid which is photosensitive and has the property of explosion. The technical product is often gray. The azide is practically insoluble in water and organic solvents. Aqueous ammonia [1] or anhydrous hydrogen fluroide [196] dissolve it as a complex; upon evaporation, the azide is recovered unchanged. Colorless needles more than 10 mm long are easily obtained from the ammonia solution [197]. In nitric acid it dissolves with chemical destruction, evolving HN_3 gas. On exposure to light, silver azide turns first violet and finally black, as colloidal silver is formed and nitrogen evolves [175,176]. As photographic emulsion, the azide is found to be 200 times less photosensitive than silver bromide, but more easily reducible by developers. The emulsions are not explosive [198].

A suspension of silver azide in boiling water decomposes with a discoloration similar to that of the photodecomposition [176]. When heated dry, the azide turns violet at 150°C and melts at 251°C to a blackish liquid. Starting at 253°C the melt evolves nitrogen gas at a rate which simulates boiling. The mass then shrinks to a brown solid and finally, at the end of decomposing, appears white. Under the microscope the particles appear as silver metal [2]. When heated rapidly, silver azide explodes at 300°C with high brisance, emitting a green light flash [1,2,176]. A partially (50%) decomposed, gray sample explodes with the same brisance at 305°C [176]. The degree of decomposition has evidently little influence on the explosive behavior. The same was found for mechanical explosion; white and gray samples are equally highly sensitive to friction and impact [199]. However, the particle size has a distinct influence on impact sensitivity; coarser samples are more sensitive [192,200]. Long needles of silver azide frequently explode when broken with a metal wire [197]. The AgN_3/N_3^- half cell assumes a standard potential of +0.384 V at 21°C; the solubility of silver azide in water was electrochemically determined as 8.4×10^{-3} g/liter at 18°C [201].

Of historic interest is a reaction in which the azide group was synthesized from hydrazine and nitrite in the presence of silver ions [19,98] (see p. 24). Most commonly, silver azide is prepared by mixing aqueous solutions of hydrazoic acid or sodium azide with silver nitrate. The product is precipitated in fine crystalline form; larger crystallites are obtained from more dilute reagents [200]. One author recommended the use of an excess of silver nitrate; another believed this would enhance the photodecomposition of the product [202]. Of more significance is the recommendation to make the azide in the dark, or at least under red light, [203,204] and to wash the product completely ion free.

To prepare 3-g batches, a solution of 3.42 g silver nitrate (slight excess) in 100 ml water is placed in a 500-ml beaker and heated to 60–70°C. The solution is stirred with a rubber-clad glass rod, and a solution of 1.3 g sodium azide in 100 ml water (60–70°C) is added within 3–4 min. The precipitate is stirred until well coagulated and then transferred to a Buchner funnel. To avoid contact with the hard funnel material, both the bottom and walls are covered with filter paper. The product is washed with water until nitrate free, then with alcohol and ether, followed by drying at 70–90°C.

The preparation [205] of 45-g batches of silver azide takes place at room temperature in a 4-liter beaker equipped with a stirrer. Silver nitrate, 51.1 g dissolved in 1 liter water, is placed in the beaker and 19.5 g sodium azide, dissolved in 1 liter water, is added with rapid stirring within 45 min. The product is isolated as above.

Precipitation of silver azide in molten salt media has also been tried by mixing the solutions of silver nitrate and sodium azide in the melt of eutectic $NaNO_3/KNO_3$ mixtures [206].

Of various complexes of silver azide known to exist in solution, [1,196, 200], only the $MeL(N_3)$ type has been isolated [164,182]; e.g., the compound $[P(C_6H_5)_3Ag(N_3)]$ is a white, crystalline solid which melts with decomposition at 170°C. It is made from a suspension of silver azide in benzene, which is treated with triphenylphosphine until soluble. The complex is then precipitated by adding pentane.

3. Azides of Gold

The normal azides of Au(I) and Au(III) have never been described, but a complex azidoaurate has been known since 1898, when Curtius and Rissom [62] reported on "Doppelsalze von Platin- und Goldaziden" (double salts of platinum and gold azides). The complexes were made in aqueous media from potassium azide and, e.g., H_2PtCl_6, according to

$$[PtCl_6]^{2-} + 6KN_3 \longrightarrow [Pt(N_3)_6]^{2-} + 6KCl$$

Curtius and Rissom discussed the nature of the above platinum complex in detail and drew an analogy to gold which reads: "Here again, by metathetic reaction of the slightly explosive potassium azide with gold chloride, is formed a highly explosive azide of gold besides potassium chloride."

The statement, taken out of context, may be misinterpreted as a claim to have prepared normal gold azide, and this conclusion was, in fact, repeatedly drawn. Mellor, for example, reviewed the (normal) inorganic azides and stated [207] that Curtius "obtained a gold azide." Rogers wrote later [208] that Curtius "considered the compound to be AuN_3 but offered no evidence to support this," and Fedoroff entered in his encylcopedia [209] that Curtius "obtained gold azide, (aurous azide), AuN_3, MW 239.22, 17.5% N." Likewise, some textbooks of inorganic chemistry mention, by implication or expression, the existence of a normal gold azide.

According to Curtius and Rissom, a solution of gold chloride, $HAuCl_4$, darkened when potassium azide was added. After evaporation, traces of metallic gold were obtained together with long, orange crystal needles. The crystals were taken up with a few drops of water. One drop of the solution exploded with unprecedented violence when heated on a metal plate.

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In an attempt to make the normal gold(I) azide, Rogers [208] reacted $HAuCl_4$ and solid sodium azide in ether. The product resembled the properties of Curtius' azidoaurate, but had the empirical composition $Na_1Au_{1.43}N_{9.05}$. Rogers considered the substance to be a new discrete phase [208], but it was more probably a mixture of Au(I) and Au(III) azido complexes [139].

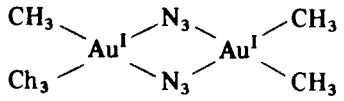
Clem and Huffman [210] studied the chemical structure of solutions containing Au(III) and azide ions. It was found that a tetraazidoaurate(III) anion, $[Au^{III}(N_3)_4]^-$, is formed when the molar ratio of Au(III) to azide is at least 1 to 10. The complex is light sensitive, especially in solution; e.g., a tetrahydrofuran solution of the tetraphenylarsonium tetraazidoaurate(III), when exposed to daylight, is quantitatively reduced to the diazidoaurate(I) complex [139]:

$$[Ph_4As]\,[Au^{III}(N_3)_4] \xrightarrow[THF]{light} [Ph_4As]\,[Au^{I}(N_3)_2] + 3N_2$$

The orange tetraazidoaurate(III) anion is chemically quite labile with a shelf life of only a few days [162]; discoloration and a separation of metallic gold accompany the decomposition [62,139,162,208]. The complex is equally labile as an explosive. The sodium and potassium salts explode violently on friction, impact, and in the flame. Rogers' substance decomposed slowly at 117° and exploded at 130°C [208]. Salts of the complex anion with large organic cations are insensitive to impact and merely deflagrate in a flame, but an explosion occurred when the tetraphenylarsonium salt was prepared with concentrated reagents, i.e., solid sodium chloroaurate, $Na[AuCl_4]$ [139].

The sodium and potassium salts of tetraazidoaurate dissolve readily in water and most organic solvents, while the large-cation salts are water insoluble.

Chemically even more labile than the azidoaurate(III) structure is the diazidoaurate(I) anion, $[Au^{I}(N_3)_2]^-$ [139], with only 2 ligands coordinated. This structure gains stability by completing to 4 the coordination number for gold. Examples are a neutral, binuclear complex of the structure,



and a L_3-type structure, $[(N_3)(Ph_3P)Au^{I}]^0$, which have both been described by Beck *et al.* [164,169].

The tetraphenylarsonium salt of tetraazidoaurate(III) is made from 2.5 mmole potassium chloroaurate, $KAuCl_4$, which is dissolved in a small quantity of water. One hundred mmole of sodium azide is added to obtain a red solution. After filtering, tetraphenylarsonium chloride is added to precipitate the orange complex. It is recrystallized from acetone-water, or methylene chloride–hexane mixtures [139]. The colorless tetraphenylarsonium salt of diazidoaurate(I), $[Ph_4As]\,[Au^{I}(N_3)_2]$, is obtained by reacting a suspension of freshly prepared gold monochloride, AuCl (0.2 g = 0.9 mmole), and sodium azide (1.5 g = 23 mmole) in water-wet methylene chloride. Upon addition of

0.2 g (=0.5 mmole) of tetraphenylarsonium chloride, a yellow solution is obtained which is filtered and precipitated with hexane [139].

4. Azides of Zinc

The normal azide, $Zn(N_3)_2$, is a white, sandy powder which is hygroscopic and has a strong tendency to decompose hydrolytically. Thus, the odor of HN_3 appears immediately when the solid is exposed to atmospheric moisture, and in time aqueous solutions separate voluminous precipitations of basic products. These basic salts are inherently poorly defined, and the "basic zinc azides" and "zinc hydroxyazides" of the literature may have analyses anywhere between $Zn(N_3)_2$ and $Zn(OH)_2$. Nevertheless, two discrete phases of the composition $(OH)Zn(N_3)$ and $Zn_3(OH)_8 \cdot Zn_2(N_3)$ were determined by X-ray analysis, but the method of preparing them was not given [160]. Recently, the existence of a dihydrate, $Zn(N_3)_2 \cdot 2H_2O$, has been suggested, with a dehydration point at 27.5°C [211].

Zinc azide explodes on impact but is markedly less sensitive than other heavy metal azides [54]; in a flame it deflagrates [54]. The temperature of explosion is near 289°C [85,115]. Basic zinc azides also explode [116].

It appears that pure zinc azide has never been isolated, because all wet methods of preparation involved water at some stage. For example, zinc metal was dissolved in hydrazoic acid; the solution supposedly contained zinc azide but separated basic salts on standing [62]. Zinc carbonate was also suspended in ethereal hydrazoic acid and agitated at room temperature for 3 days. The product was then extracted with cold water to yield an azide which was not free of H and O [54, 143]. Basic products were also obtained by distilling hydrazoic acid onto zinc carbonate [212] or hydroxide [116], or by reacting zinc sulfate and barium azide solutions [73]. Hydrolysis in these aqueous solutions may be retarded by precipitating the azide with acetone [213].

Using the dry Wislicenus process, ^{15}N-doped zinc azide was made by reacting zinc amide with nitrous oxide at 180°C for 96 hr [85]. The product can be considered pure $Zn(N_3)_2$, but an equimolar amount of zinc hydroxide is admixed which was not separated.

A tetraazidozincate anion, $[Zn(N_3)_4]^{2-}$, was isolated as the cesium, tetraethylammonium, and tetraphenylphosphonium salts. It appears to be stable in aqueous media, as aquation or hydrolytic decomposition have not been reported. In fact, the cesium salt grows into large crystals from aqueous solutions. The compounds are white solids which are not impact sensitive; depending on the nature of the cation, they are soluble in water or polar organic solvents.

Cesium tetraazidozincate, $Cs_2[Zn(N_3)_4]$, for example, is made by dissolving zinc carbonate in excess hydrazoic acid. To this is added a fivefold excess of cesium azide. Upon slow evaporation at room temperature the complex separates as crystals [148].

Tetraethylammonium tetraazidozincate, $[(C_2H_5)_4N]_2[Zn(N_3)_4]$, is formed when 0.1 g tetraethylammonium tetrachlorozincate and 1 g sodium azide are

shaken for [illegible] with approx. 20 ml acetone. The filtered solution is precipitated with ether. For purification, a nitromethane solution of the product is reprecipitated with ether (MP, 193°C) [158].

Tetraphenylphosphonium tetraazidozincate, $[(C_6H_5)_4P]_2[Zn(N_3)_4]$, results when an aqueous solution of 1 g zinc sulfate heptahydrate and 5 g sodium azide is precipitated with 0.5 g tetraphenylphosphonium chloride in water. The white precipitate is washed with water/alcohol 1:1 [139].

A mixed zinc azido complex containing 2 pyridines was first made by Dennis and Isham [192]. Strecker and Schwinn [188] interpreted its structure as azide salt of a complex zinc cation: $[Zn(Py)_2]^{2+}(N_3)_2^-$. A recent study of Agrell [214], however, suggests the more conclusive structure of the neutral complex, $[(Py)_2Zn(N_3)_2]^0$. It is made by mixing equimolar solutions of sodium azide and zinc nitrate; pyridine is then added to the warmed mixture until all is dissolved. Upon cooling, the complex separates in crystalline form [214].

5. Azides of Cadmium

The normal cadmium azide, $Cd(N_3)_2$, is a white, crystalline solid which is hygroscopic and tends to hydrolyze. Thus, the salt turns yellow when exposed to atmospheric moisture. The azide dissolves in water, probably as an aquo complex. Upon standing, the solution turns yellow and slowly precipitates basic products [62,215,216]. Excess azide ion in the solution leads to the formation of various azido complexes with a maximal ligand number of 5 [217,218]; excess pyridine forms a diazidodipyridine complex [62,188,219,220].

While cadmium azide is definitely an explosive, there is no agreement on its sensitivity, probably because the various materials were not well defined. Curtius and Rissom [62] found it insensitive to impact; when heated, it decomposed with sputtering, but without explosion. Wöhler and Martin [115] saw the azide explode at a mechanical shock of 18.5 kg/mm² (lead azide, 4.5; thallous azide, 17.5). Birckenbach found it extremely dangerous, as it exploded violently when scratched with a plastic spatula, and detonated when heated [215]. Kahovec and Kohlrausch [73] abandoned working with CdN_6 after a sample exploded spontaneously. Spontaneous explosion of a crystal growth solution was reported by Bassiere [216]. Cadmium azide decomposes thermally with explosion occurring between 291 and 330°C, depending on such factors as sample size [115], crystal size [158], and loading density [221].

Cadmium azide is made in aqueous media, usually by dissolving the carbonate or hydroxide in hydrazoic acid [62,73,115,157,215]. The product is crystallized from the yellow, filtered solution by evaporating or cooling to yield slightly yellow crystal needles of 98.5% purity. A white product of higher purity (99.5%) is obtained by keeping the reaction mixture acidified with strong hydrazoic acid [215].

Curtius and Rissom [62] reacted cadmium azide with pyridine to obtain a colorless complex containing two azide and two pyridine ligands. Stoichiometric amounts of pyridine and sodium azide are mixed with 0.5 M cadmium nitrate;

the precipitate may be redissolved in hot (90°C) pyridine from which crystallizes upon cooling [215]. Strecker and Schwinn [188] extended the study to other ligands such as NH_3 and ethylenediamine; the structure of the compounds was qualitatively determined from chemical reactions as the normal azide of complex cations, e.g., dipyridine cadmium azide, $[Cd(Py)_2]^{2+}(N_3)_2$. More recently, Agrell found physical evidence (X-ray and infrared data) which points to a neutral structure for the complex, i.e., $[Cd(Py)_2(N_3)_2]^0$ [219, 220]. Like $Cd(N_3)_2$, these complexes are explosive and tend to hydrolyze.

Another complex, which was isolated as the tetraphenylphosphonium salt [139, 173, 222], has the possible binuclear structure $[Cd_2(N_3)_5]^-$.

6. Azides of Mercury

Mercury(II) azide, $Hg(N_3)_2$, is a colorless, crystalline explosive which detonates with high brisance on friction, impact, and heat shock. Its explosive sensitivity depends largely on the particle form, of which two distinct types have been qualitatively described [223]. The first, consisting of compact, small crystallites of 60–80 μm diam. [224], is relatively insensitive and has without mishap been coarsely powdered [223] or ground in nujol [12]; it explodes on impact of a 500-g weight dropping from 65 mm [224]. The second, in the form of long, thin needles, explodes at the slightest provocation [13,224] or even spontaneously [223-226].

$Hg(N_3)_2$ is somewhat photosensitive and turns yellow in bright daylight, owing to the appearance of colloidal mercury. It also decomposes thermally [2], with gas evolution starting at 212°C, followed by discoloration at 220°C and explosion at 300°C. The compound is slightly soluble in cold water (0.257 g in 100 g solution at 20°C) [223]; in hot water it dissolves more readily, without noticeable hydrolysis. It also dissolves in ethanolamine, apparently without chemical reaction [227], and in hydrofluoric acid, as a cation complex. Upon evaporation of the acid, the azide appears unchanged [196].

$Hg(N_3)_2$ has been made by dissolving mercury(II) oxide in hydrazoic acid [13, 225, 226]:

$$HgO + 2\,HN_3 \longrightarrow Hg(N_3)_2 + H_2O$$

To separate the product from unreacted HgO, the azide is dissolved by heating and then filtered. It recrystallizes as the above-mentioned, highly sensitive needles which have to be handled with extreme caution; e.g., a large particle, slowly sinking in a water-filled beaker, exploded when touching the bottom [13]. Likewise, crystals adhering to the wall could not be removed without explosion. It is essential to move the liquid constantly with a stirrer made of a soft material [13], as slow cooling of an unstirred solution leads invariably to explosion [224].

The compact crystal form is prepared more safely by precipitating at room temperature a concentrated solution of mercury(II) nitrate or chloride with sodium azide. The product may be separated by centrifuging [12].

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Amo... complex mercury(II) azides a colorless, explosive dipyridine diazidomercury(II) of the possible structure $[Hg^{II}(Py)_2(N_3)_2]^0$ is precipitated when water is added to a solution of mercury(II) nitrate in pyridine [138]. A triazidomercurate(II), $[Hg^{II}(N_3)_3]^-$, is obtained from mercury(II) nitrate and excess sodium azide in acid media and isolated as the tetraphenylphosphonium salt [139,222,238].

Like mercury(II) azide, mercury(I) azide, $Hg_2(N_3)_2$, is a colorless, solid explosive, which is precipitated from aqueous media as a crystalline powder of high sensitivity. It explodes with high brisance on impact of a 500-g weight dropping from 60 mm (lead azide, 430 mm; silver azide, 410 mm) [229]. Heated at 283°C it explodes in 178 sec, and at 292°C in 75 sec [115]. Slow thermal decomposition leads to discoloration at 170°C, melting with decomposition at 230°C, and ignition at 400°C [230]. Its photosensitivity is higher than that of mercury(II) azide: Exposed to daylight it turns yellow, then orange, brown, black, and finely separates droplets of gray mercury [175]. The mechanism does not involve disproportionation of the Hg(I) state [176].

Thin crystal needles should be avoided as they are extremely sensitive and would, upon breaking, set off the whole batch [225,226]. Small particles are obtained by rapidly precipitating a concentrated mercury(I) nitrate solution with sodium azide and centrifuging the product [225].

K. AZIDES OF THE IIIA ELEMENTS

1. Azides of Boron

Normal boron azide, $B(N_3)_3$, is a white solid and is chemically not very stable. The compound explodes when shocked mechanically or thermally and has a strong tendency to decompose hydrolytically. The only known synthesis starts from hydrazoic acid and diborane and yields the boron azide contaminated with boron hydrogen azides. The compound is ether soluble [231]:

$$3HN_3 + BH_3 \longrightarrow B(N_3)_3 + 3H_2$$

In a closed system, an ethereal solution of hydrazoic acid is frozen with liquid nitrogen, and diborane (BP, -92.5°) is condensed in. The mixture is allowed to slowly warm up to room temperature. After melting, the fluid is rapidly stirred. Reaction starts at -20 to -10°C with gas evolution and continues for about 1 hr. The hydrogen is then pumped off, and the reaction recommences. Reaction and pump cycles are repeated until 95% of the total hydrogen has been removed.

The isolation of the product is extremely difficult as the boiling temperatures of product and solvent are close; the boiling liquid also tends to explode.

The properties of lithium tetraazidoborate, $Li[B(N_3)_4]$, resemble those of normal boron azide. It is synthesized, apparently in a two-stage reaction, from lithium borohydride and hydrazoic acid:

$$LiBH_4 + 4HN_3 \longrightarrow LiB(N_3)_4 + 4H_2$$

Excess ethereal hydrazoic acid is condensed onto a frozen (liquid nitrogen) ethereal solution of $LiBH_4$. The solid mixture is allowed to warm up; between -116 and -80°C, H_2 is evolved and LiN_3 precipitates:

$$LiH \cdot BH_3 + HN_3 \longrightarrow LiN_3 + BH_3 + H_2$$

Near 0°C, H_2 is again evolved and ether-soluble $LiB(N_3)_4$ is formed:

$$LiN_3 + BH_3 + 3HN_3 \longrightarrow LiB(N_3)_4 + 3H_2$$

After pumping the solvent off, the product is obtained as a white solid [232].

2. Azides of Aluminum

Aluminum azide, $Al(N_3)_3$ is a white, crystalline solid which is chemically not very stable. Freshly prepared samples deflagrate in the match test with sputtering, and explode on impact. When exposed to atmospheric moisture, the compound decomposes hydrolytically within minutes to yield insoluble products with little or no explosive sensitivity [233]. Similarly, aluminum hydroxide is immediately precipitated when sodium azide is added to solutions of aluminum salts [135]. In tetrahydrofuran, $Al(N_3)_3$ dissolves with solvation; such solutions are useful as azidation agent in organic synthesis [234].

The compound was first prepared by adding HN_3 gas to a frozen (liquid nitrogen) solution of aluminum hydride in ether and thawing the mixture to room temperature [233]. THF solutions of $Al(N_3)_3$ are made by refluxing $AlCl_3$ and NaN_3 for 5 hr in benzene media. The precipitate of $Al(N_3)_3$, NaCl, and excess NaN_3 is separated and digested with THF to extract the aluminum azide, which is then precipitated with ether [61,234]. Better yields (89%) are obtained by digesting a mixture of 8 g $AlCl_3$ and 17.5 g NaN_3 in THF at room temperature for 15 hr [82]. Azidation of aluminum chloride with trimethylsilyl azide was also tried but the products were only partly azidized [111].

Sodium tetraazidoaluminate, $Na[Al(N_3)_4]$, is a white, crystalline solid with properties similar to $Al(N_3)_3$. When heated it does not explode below 300°C. Impact sensitivity (50% fire level) is reached at 65 mm (2-kg weight). The complex is soluble in hydrazine without decomposition; in THF it dissociates and separates NaN_3 [61]. To prepare the compound, solutions of $AlCl_3$ in benzene and of NaN_3 in THF are combined and stirred overnight at room temperature. The liquid phase is then distilled to remove THF. Further dilution with benzene, and additional distillation to remove all THF, yield the product in pure form [61].

The lithium salt, $Li[Al(N_3)_4]$, was made by digesting at room temperature a mixture of lithium aluminum hydride and hydrazoic acid in ether [61].

3. Gallium Azide

According to the reaction

$$3HN_3 + GaH_3 \longrightarrow 3H_2 + Ga(N_3)_3$$

the normal gallium azide may be formed. Wiberg and Michaud [235] combined ethereal solutions of gallium hydride and hydrazoic acid in the frozen state; the mixture was allowed to warm up to room temperature. The product was not completely azidized; a typical analysis showed the composition $GaH_{0.2}(N_3)_{2.8}$.

4. Thallium(I) Azide

In the periodic table thallium(I) azide, TlN_3, is flanked by mercury azide and lead azide and, like these two, it explodes with high brisance when shocked mechanically or thermally. It is easier to handle, however, owing to a lower impact sensitivity (see [115] and [236] for figure values) and a much lower photosensitivity. Also, the general solution chemistry of the Tl^+ ion is simpler than that of Hg^+, Hg^{2+}, and Pb^{2+}, and chemical complications such as hydrolysis, basic salts, complexing, and exploding crystal growth solutions need not be considered. Consequently, TlN_3 is often chosen in explosives research as a model azide. (By the same token, its low impact sensitivity renders it unfit for technological applications.)

TlN_3 has one nasty property which requires attention: Its sensitivity to friction depends on the sample thickness and is highest in very thin layers. Pointed out by Wöhler and Martin [115] as early as 1917, this fact went grossly unnoticed and has resulted in several unnecessary accidents in laboratories. Thallium(I) azide should be handled with the same safety precautions that apply to lead azide.

TlN_3 is one of the few metal azides that melt (MP *in vacuo*, 330°C) prior to decomposition. At 340°C it begins to sublime, evolves gas at 370°C, and explodes at 430°C, leaving silver-white thallium metal as residue [2]. It is only slightly soluble in cold water.

The compound is obtained very easily by admixing a soluble azide to an aqueous thallium(I) salt solution. The product precipitates immediately as a straw-yellow crystal powder. Larger crystals are obtainable by cooling hot, saturated aqueous solutions [62]. Combinations such as thallium sulfate/potassium azide [237] and thallium nitrate/ammonium azide [61] may be used for the preparation. This author prefers thallium perchlorate and sodium azide, because favorable solubility products of the ions involved and the absence of hydration lead to a material that is free of coprecipitated ions. For example, to a stirred solution of 200 g $TlClO_4$ in 1600 ml water is admixed 45 g sodium azide dissolved in 150 ml water. The dense precipitate is washed with cold water until perchlorate free, and then with acetone. Practical yield, 152 g. The product should be stored completely dry as the damp material tends to discolor [236].

By dissolving thallium(III) hydroxide in hydrazoic acid, Dennis and Doan [237] obtained a yellow, highly explosive solid which, in contrast to TlN_3, is soluble in water with slow decomposition. Although the ratio of Tl(I) to Tl(III) was found to be >1, it was considered to be thallous-thallic azide, $Tl^+[Tl^{3+}(N_3)_4]^-$, assuming that excess Tl(III) had been reduced during analysis by hydrazoic acid. This argument is not convincing, especially since a substance

containing two oxidation states of thallium in the same molecule should have other properties than those described by Dennis and Doan.

L. AZIDES OF THE IVA ELEMENTS

The azides of group IVA display properties which are, for the most part, symptomatic of covalent element-to-azide bonds. Evidence of ionic influence appears late in the group and remains small, for example in the ability to form an azido complex of Sn(IV). Even the azides of lead, the most electropositive IVA metal, are predominantly covalent, although the ionic bonding component is sufficiently strong to form the only divalent normal azide of the group.

Individually, the IVA azides display a wide range of reactivities. Some C and Si azides, for example, decompose at or below room temperature while others, offering synthetic prospects, transfer the azide group intact and readily. In another area, the knowledge of metalorganic compounds is gaining valuable input from structural nuances that are displayed by the organyl azides from Si to Pb. Interest in these areas has arisen fairly recently while lead(II) azide, in contrast, has continued to inspire and challenge explosives research and technology almost since the beginning of the century.

1. Azides of Carbon

Only three "inorganic" carbon azides are discussed here, with carbon-to-azide bonds and one carbon per molecule. The parent compound, $C(N_3)_4$, is not known, but Müller and Dehnicke [238] were able to isolate a triazidocarbonium hexachloroantimonate, $[C(N_3)_3]^+(SbCl_6)^-$. The cation structure was elucidated from infrared data and appears to be analogous to the guanidinium ion. The compound is described as a slightly hygroscopic, yellowish-white solid which dissolves in polar solvents and explodes on impact and heat shock. It decomposes thermally after melting at 145°C. Synthesis [238] was achieved by refluxing for 4 hr a mixture of $Sb(N_3)Cl_4$ [239,240] and carbon tetrachloride.

Two other azides of carbon, cyanogen azide and carbonyl azide, are neutral molecules. In the nomenclature that was used for treating Fig. 1, they would appear as hetero azides. Cyanogen azide, $NC-N_3$, was described in 1964 by Marsh and Hermes [241] as a colorless oil which is a lachrymator and explodes at the slightest provocation of mechanical, electrical, or thermal shock. (In the older literature [242-245], the structure $NC-N_3$ was erroneously assigned to other substances.) In spite of its noxious properties, the compound has become an important synthetic reagent in the organic laboratory; its isolation is not required, as preparation and reactions are conducted in solution (5%) or as a gas at reduced pressure [246-248]. $NC-N_3$ can be handled safely under these conditions, but when selecting a solvent, it must be considered that the azide may separate and explode if low-boiling solvents evaporate, saturated solutions

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are cooled, or the solvent is frozen. To make cyanogen azide, finely powdered sodium azide is metathetically reacted with cyanogen chloride or bromide in dry organic media. The temperature range is 0–12°C; reaction times depend on the solvent. For details, see references [246–249].

The other heteroazide of carbon, carbonyl azide, $O{=}C(N_3)_2$, displays an enhanced sensitivity. It detonates on mild mechanical or thermal shock and is even set off when exposed to bright daylight. The compound was synthesized in 1894 from carbazide and nitrite [250], but owing to its instability has found no applications.

2. Azides of Silicon

The first silicon azide, $Si(N_3)_4$, was described in 1954 [251]. Since then, over 30 compounds have been reported, including the purely inorganic $H_3Si(N_3)$ and $D_3Si(N_3)$ [252]. The rest are organosilicon azides (silyl azides) of the general structure $R_xSi(N_3)_{4-x}$ [71,72,111,253–267]. All silicon azides are highly sensitive to hydrolysis but otherwise cover a wide range of stabilities. A few typical examples are given in Table XIII. The more stable silyl azides, especially trimethylsilyl azide, $(CH_3)Si(N_3)$, have found use as azide transfer agents for inorganic (see beryllium azide, p. 38) and organic syntheses. Trimethylsilyl azide is accessible through a number of synthetic routes [254,256–258,263] of which the trimethylchlorosilane/sodium azide process appears superior, particularly when conducted in HMPT (hexamethylphosphortriamide, $OP[N(CH_3)_2]_3$) media. For details, see reference [266].

3. Azides of Germanium and Tin

As electropositivity increases, the azides of the heavier IVA elements shift toward a more hydrophile behavior. This pattern is qualitatively noticeable in the triorganyl element azides (see Table XIV for trimethyl compounds). The triphenyl compounds display a similar behavior [9,261,272]. Basically, all $R_3El(N_3)$ compounds are accessible from the respective chloro compounds and sodium azide in ether/water media [273].

Table XIII. Stabilities of Some Silicon Azides

	MP (°C)	BP (°C)	Stability	References
$Si(N_3)_4$			Spontaneous explosion at 0°C	251
$H_3Si(N_3)$	−81.8	+25.8	Thermal decomposition at room temperature	252
$CH_3Si(N_3)_3$		70 (20 mm)	Spontaneous explosion at 70°C/20 mm	259
$(CH_3)_3Si(N_3)$	−95	+96	Burns without explosion; thermal decomposition above 300°C	71, 262

Table XIV. Properties of IVA-Element Trimethylazido Compounds

	MP (°C)	BP (°C)	Stability	Behavior toward water	References
$(CH_3)_3Si(N_3)$	−95	+96	Burns without explosion; dec. above 300°	Rapid hydrolysis	71, 262
$(CH_3)_3Ge(N_3)$	−65	+136	Burns with deflagration; dec. above 300°	Insoluble; hydrolizes in atm. moisture	262, 264, 269
$(CH_3)_3Sn(N_3)$	+121		No observations	Soluble; negligible hydrolysis	262, 264
$(CH_3)_3Pb(N_3)$			Dec. above 200°	Soluble; negligible hydrolysis	262

In the hexaazidostannate(IV), $[Sn(N_3)_6]^{2-}$, the first IVA azido complex appears. In spite of six azido groups, the complex is not very sensitive. The sodium salt deflagrates when shocked thermally but is stable to impact [275]; its salts with large organic cations are stable to both stimuli [158,222,228]. There are also known two mixed tin azides, $ClSn(N_3)$ [132] and $Cl_2Sn(N_3)_2$ [271], which are white, hydrolysis-sensitive solids with explosive properties.

4. Azides of Lead

Lead forms various azides in its tetravalent state like the other IVA elements, but is the only member of the group to also form a normal azide in its lower (Pb^{2+}) oxidation state.

$Pb(N_3)_2$ is better known than almost any inorganic azide; in fact, the number of publications written on it is surpassed only by sodium azide and HN_3. This is undoubtedly because lead azide has been used for nearly 60 years as an effective, if sometimes problematic, primary explosive. It is not the first azide to be considered for military use; the feasibility of silver azide was explored in Germany as early as 1904. In 1911, lead azide was suggested as a military explosive by Wöhler [224], and being technically and economically superior [275] to mercury fulminate, has gradually replaced the latter.

The chemistry of making lead azide is quite simple. It is precipitated in a metathetic reaction by mixing solutions of a lead salt and sodium azide:

$$Pb^{2+} + 2NaN_3 \longrightarrow Pb(N_3)_2 + 2Na^+$$

In practice, however, there are factors such as purity, polymorphism, particle form, etc., which are of great technological concern as they may influence the explosive behavior and the storage compatibility of the product. Controlling these factors is essential, and thanks to continued research, our knowledge of the underlying principles has advanced in at least some areas. Others lag behind, owing in part to a lack of appropriate study materials. From the viewpoint of

making research samples in the laboratory, the following points deserve increased attention in present and future projects.

Lead azide is a white, crystalline solid which is sparingly soluble in water [276]; its solubility may be enhanced by complexation [157,276]. Hydrolysis at room temperature is negligible [197]. The compound is somewhat photosensitive and, unless handled under yellow light, appears buff or gray [175,176]. It is highly sensitive to impact, heat shock, and friction and explodes with high brisance [197]. Thermal decomposition leads to explosion above 345°C [2,176].

Pb^{2+} ions in aqueous solution are hydrated as a tetraaquocomplex, $[Pb(H_2O)_4]^{2+}$; in addition, hydroxoaquo ions, $[(OH)Pb(H_2O)_3]^{+}$, are formed in the presence of free $(OH)^-$ ions. Lead hydroxoaquo salts are usually very insoluble and prone to precipitate basic salts [277]. Lead azide, for example, has at room temperature a solubility product of 2×10^{-9} [278,279], and basic lead azide, $(OH)Pb(N_3)$, of 3×10^{-15} [278]. When making lead azide under such conditions, for example in presence of $(OH)^-$-releasing additives, it should be considered that the product is $(OH)^-$ doped.

Not yet understood is the phenomenon of spontaneous explosion in saturated azide solutions, which has been observed during crystallization of cadmium [216], copper(II) [224], mercury(II) [224], and lead [176,223,224, 280,286] azides, in both aqueous and gel media [281]. Explosions occurred at elevated as well as room temperatures [281,282]. Research so far has aimed at avoiding [282,283] or producing [284,285] the effect. In lieu of more solid advice, it may be said that the reported explosions evidently occurred in highly complexed solutions, usually containing the heavy-metal ions in excess.

Lead azide exists as four polymorphic forms [287] of which the orthorhombic α-lead azide is the most stable [276]. In fact, α-lead azide is the only acceptable form for technological applications. Presently, the state of the art of making the polymorphs can be summarized as follows: α-lead azide is the main product of precipitation, with traces of the other forms present [288]. The monoclinic [276] β-form is stable when dry, but recrystallizes as the α-form [276,289]. The presence of organic dyes (eosin, neutral red) at the precipitation enhances formation of β-lead azide [276]; the presence of hydrophile colloids inhibits it [276,287]. The monoclinic [287] γ-form, apparently less stable than α and β [289], is obtained from pure reagents at a pH of 3.5–7 [287] or in the presence of polyvinyl alcohol [289]. The triclinic δ-form precipitates from pure reagents between pH 3.5 and 5.5 [287]. No method is presently available to yield a single polymorph exclusively, but the crystals differ sufficiently in shape to allow hand selection under the microscope [287,288].

The growing of single crystals is an art which, especially with azides of explosive sensitivity, exceeds common skills and techniques and is treated separately (Chapter 2).

Ionic doping of crystalline samples is presently achieved by coprecipitation [291–293]. Thin films are doped by gasing lead alloys with HN_3 [294]. No techniques have been reported for quantitatively controlling dopant concentrations or occupying specific lattice sites.

The following are examp
use.

α-Lead Azide, 20-g Batch. A 600-ml lead acetate solution (5% w) is placed in a 1500-ml beaker. With stirring, 500 ml sodium azide solution (2%) is slowly added from a dropping funnel. At the first permanent precipitation, the addition is interrupted to inspect a drop under the microscope. If still amorphous, stirring is continued without further addition until crystals form. When all is added, the product is washed with water and alcohol on filter paper and dried at room temperature *in vacuo*. Yield, 20.5 g [205]. The operation should be conducted under amber light.

Dextrinated Lead Azide, 20-g Batch. A 500-ml lead nitrate solution (6%), containing 1 g dextrin, is precipitated at 45–50°C with 500 ml sodium azide solution (2%) containing 0.3 g sodium hydroxide. To prevent the formation of larger crystals, stirring is continued until room temperature is reached. Yield, 20.8 g [205].

β-Lead Azide. Solutions of lead nitrate (20%) and sodium azide are, at room temperature, run into water containing 0.02% eosin [276]. The crystals are best handled as single specimens as they are extremely sensitive; breaking one will set off the whole batch.

γ- and δ-Lead Azides. The two modifications are precipitated together from unstirred solutions at room temperature. A 50-ml solution containing 10 mmole nitric acid and 20 mmole lead nitrate is diluted to 250 ml, and 50 ml 20-mM sodium azide is admixed and swirled once. After 3 days, the crystals are collected and separated by hand [287].

Lead azide is also obtainable from lead nitrite and hydrazoic acid [295]. Unlike simple metathesis, nitrite and azide react chemically to yield two inert gases, N_2 and N_2O, besides water, and the precipitated lead azide is, therefore, free of any coprecipitated ions. In practice, lead nitrite is first made by bubbling N_2O_3 into a suspension of lead oxide in water, and the yellow solution is then reacted with hydrazoic acid as alcoholic solution, or as gas carried with nitrogen:

$$PbO + N_2O_3 \longrightarrow Pb(NO_2)_2$$

$$Pb(NO_2)_2 + 4HN_3 \longrightarrow Pb(N_3)_2 + 2N_2 + 2N_2O + 2H_2O$$

In another method lead azide is precipitated in molten salt media [296], such as the eutectic mixture of $KNO_3/LiNO_3$ (MP, 129°C). Since lead nitrate (A) and potassium azide (B) dissolve in molten nitrates, but lead azide does not, separate solutions of A and B in the melt are combined to precipitate the latter. The solidified melt is then leached out with water at room temperature.

Basic azides of various $(OH)^-$ contents have been described, displaying less explosive power than lead azide. The compound $(OH)Pb(N_3)$, for example, merely deflagrates. It was made by Wöhler and Krupko by way of hydrolysis: Air was bubbled through a hot suspension of lead azide in water until the expelled HN_3 had neutralized, via titration, the calculated amount of the base [176].

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Other basic azides were made by treating lead azide with sodium hydroxide solution, precipitating lead salts with sodium azide/hydroxide mixtures. Altogether, nine phases are distinguished by X-ray analysis [297,298]. A lead(II) azide chloride, $ClPb(N_3)$, is similarly obtained from lead nitrate and azide/chloride mixtures [270,292] as a white solid of reduced explosivity relative to lead azide.

Among the azides of Pb(IV), the parent compound, $Pb(N_3)_4$, is not stable. Attempts to make it from PbO_2 and hydrazoic acid in aqueous media yielded red solutions or dark red needles that tended to explode or decomposed quickly to lead(II) azide and nitrogen [299]. The molecule may be stabilized, however, as the hexaazidoplumbate(IV) complex, $[Pb^{IV}(N_3)_6]^{2-}$, and isolated with large organic cations [139,222,228]. The red solids are not explosive, dissolve in dichloroethane, and are photosensitive (decoloration, reduction to Pb^{2+}) [222]. Of higher chemical stability than other elements in group IVA are the triorganyl azides of lead(IV). Trimethyllead azide was already mentioned (Table XIV). Triphenyllead azide [9,261,300,301] melts at 187.5°C, decomposes at 219°C, and burns without explosion.

M. AZIDES OF THE VA ELEMENTS

In a general sense, the azides of the VA elements resemble the respective chlorides but are higher in volatility and less thermostable. Two of them, ammonium and hydrazine azides, represent the lowest oxidation states of nitrogen and are water-soluble salts. They are of technological interest and have been well investigated. With the exception of another salt, hydroxylamine azide, the rest of the group are either highly explosive hetero azides or (less explosive) metalorganic azides. Knowledge of them is still restricted to molecular parameters and a few general properties.

1. Ammonium Azide

This compound, of the interesting empirical composition N_4H_4, has the properties of a typical ammonium salt. At 20°C, 100 ml water dissolve 20.16 g; 100 ml methanol, 3.27 g; and 100 ml ethanol, 1.06 g [47]. It is easily recrystallized from hot methanol or precipitated with ether.

Like ammonium chloride, N_4H_4 dissociates thermally below the melting point according to $NH_4N_3 \rightleftharpoons HN_3 + HN_3$, but the tendency here is so pronounced that the vapors are completely dissociated at room temperature [302], and the substance volatilizes quickly when left uncovered [1,62].

The thermal dissociation of N_4H_4 is frequently mistaken for sublimation. It has been reported with a note of surprise, for example, that the salt explodes when heated in a sealed system, but not in open air [303,304]. These explosions stem from a pressure build-up of free HN_3 in the vapor phase (see hydrogen

azide, p. 25). Likewise, older reports on the temperatures of thermal decomposition [62], sublimation [303,304], and deflagration [225,226] do not discount the presence of free HN_3.

N_4H_4 is made by simple metathetic reaction in liquid, solid, or gaseous media which may involve distillation or precipitation. For example, equimolar amounts of ammonium chloride and sodium azide may be distilled with an equal quantity of water. At 160°C pot temperature, the product volatilizes with water vapors and solidifies in the condenser tube which should, therefore, be at least 1 inch wide [305]. Equally clean and safe is a gas-phase reaction which requires, however, the preparation of hydrazoic acid gas. The reaction takes place in a long, 1-inch-wide glass tube which has two inlet tubes with orifices 20 inches apart, and a vent. The HN_3 gas, carried with nitrogen, and excess ammonia stream in and precipitate the product as fine needles [39]. N_4H_4 is also precipitated when ammonia gas is bubbled into an ethereal hydrazoic acid solution [86]. The product stays in solution when HN_3 vapors, carried with nitrogen, are bubbled into aqueous ammonia [306].

The following procedures have also been reported as advantageous, but are in fact inferior: Larger batches were made by mixing equimolar amounts of sodium azide and ammonium acetate as saturated solutions; upon cooling to 5°C, N_4H_4 separated in low yield (approx. 25%). Additional crystallizations from the mother liquor were contaminated with sodium acetate [307]. Or, a distillation method uses dimethylformamide as a vehicle to react and distill sodium azide and ammonium sulfate. The procedure is cumbersome because clogging of the condenser could not be controlled satisfactorily, in spite of elaborate equipment [308]. Not recommended is a dry method in which sodium azide and ammonium nitrate are heat treated, and the product is "sublimed" off at 200°C. The vapor phase contains free HN_3 which tends to explode above room temperature (see p. 25). Reportedly, 5-g batches were made safely, but a 50-g batch exploded at 158°C [303].

Alkylammonium azides, such as the tetramethyl salt, $[(CH_3)_4N]N_3$, are accessible through mixing the respective iodides with silver azide [309] or, less hazardously, by neutralizing the respective hydroxides with hydrazoic acid to pH 8 [310]. Generally, they are more stable than ammonium azide, as free HN_3 is not formed through dissociation. They burn in a flame without explosion and are insensitive to mechanical and thermal shock.

2. Hydrazine Azide

Curtius [197] made hydrazine azide, $(N_2H_5)N_3$, in 1891 from hydrazoic acid and hydrazine, both of which he had discovered in the two preceding years. Today, the compound has found application in rocket fuel technology.

N_5H_5 is a very hygroscopic, extremely soluble salt: at 23°C, 100 g water dissolve 190 g. It also dissolves in methanol (6%) and ethanol (1%); it is insoluble in ether [311]. It is not sensitive to impact [311] but explodes on heat shock

[197]; after melting at 70.5°C [52] it decomposes at about 90°C [312]. In a flame it burns without explosion [197].

If hydrazoic acid is available, hydrazine azide is made by simply admixing the acid with an equimolar quantity of hydrazine, either by bubbling in the HN_3 gas [52] or by using aqueous or ethereal HN_3 solutions. In the latter case, the hydrazine azide is precipitated [197,311]. The preparation from sodium azide and hydrazine salt is more convenient. According to one source [313], 17 g hydrazine sulfate, 17 g sodium azide, and 4 g hydrazine are refluxed in 2 liters *n*-butanol at 117°C for 15 min. The liquid phase is then separated and cooled to 5°C when N_5H_5 is precipitated.

3. Hydroxylamine Azide

This compound, $(NH_3OH)N_3$, is made by neutralizing hydroxylamine with hydrazoic acid and is described as a white, volatile solid which is water soluble and melts at 66°C [192].

4. Nitrosyl Azide

$ON—N_3$ is a hetero azide in which four nitrogens are linked together with covalent bonds. The yellow liquid (MP, -66°C) decomposes thermally above -50°C. It was obtained in low yield (6%) from NOCl and sodium azide *in vacuo* at low temperature; frequent explosions occurred during the experiments [314].

5. Nitryl Azide

$O_2N—N_3$ was made under similar conditions from a nitryl salt and lithium azide, but was not isolated. In acetonitrile solution it decomposed above -10°C [63].

6. Azides of Phosphorus

These compounds, obtainable from the respective chlorides and lithium or sodium azides, have covalent phosphorus-to-nitrogen bonds. Properties are summarized in Table XV. Triphosphonitrilic hexaazide is a colorless, explosive oil

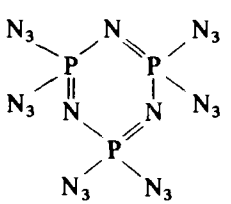

Table XV. Properties of Monomeric P(III) and P(V) Azides

	Properties	Explosivity	References
$F_2P—N_3$	Gas, spontaneously flammable	Spontaneous explosions	64
$(CF_2)_2P—N_3$	Liquid, thermal dec. below 20°C	Spontaneous explosions as low as liquid N_2 temp.	65
$(C_6H_5)_2P—N_3$	Solid, thermal dec. at 13.6°C	Not reported	315
$(C_6H_5)_2P(O)N_3$	Liquid, BP 137°C at 0.05 mm	Not impact sensitive	9, 316
$(CH_3)(C_6H_5)P(O)N_3$	Not reported	Not impact sensitive, burns without explosion	317

(thermal decomposition, 250°C) which is sensitive to heat shock, impact, and friction. It is made [319] from the chloride and hydrazine-activated sodium azide in acetone. The compound is soluble in organic solvents, insoluble in water, and does not hydrolyze.

The reaction of antimony tetrachloride azide, $SbCl_4N_3$, with PCl_3 in water-free solvents yields a highly unstable, crystalline solid of the composition $[P^V(N_3)_4]^+(SbCl_6)^-$. The extremely sensitive compound explodes on thermal and mechanical shock and sometimes spontaneously [320]. Gradual introduction of methyl groups stabilizes the cation to the point that the monoazido compound, $[(CH_3)_3PN_3]^+(SbCl_6)^-$, is nonexplosive and not very moisture sensitive [321].

7. Azides of Arsenic

The arsenic azides are moisture sensitive, and although metallic As dissolves in hydrazoic acid, no N_3-containing products can be isolated [135]. More stable are organoarsenic azides of which the dimethyl compound, $(CH_3)_2AsN_3$, is best known [70,322,323]. The colorless liquid, BP = 163°C/742 mm, is slightly hygroscopic and photosensitive but not explosive. It is soluble in organic solvents and is made from the chloro compound and LiN_3 [70], or from the iodide and AgN_3 [323]. A cationic azide of As(V), $[(CH_3)_3AsN_3]^+$, was isolated as the hexachloroantimonate [321]. Like the respective phosphorus compound, the colorless needles are not very moisture sensitive and decompose above 110°C.

8. Azides of Antimony

Metallic Sb dissolves very slowly in hydrazoic acid, and owing to hydrolysis, no azide-containing products can be isolated [135]. Some organoantimony azides are known, such as the liquid $(C_6H_5)_2SbN_3$, [324], which resembles the respective P and As compounds. A low azidized compound of Sb(V), the yellow

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crystalline $SbCl_4N_3$ [325,326], explodes on mechanical and thermal shock. Thermal decomposition starts at 107°C and leads at 131°C to melting, sometimes with explosion. The compound is obtained by azidation of antimony pentachloride with chlorine azide [325] or with trimethylsilyl azide [326]. Equally explosive is the yellow anion $[SbCl_5(N_3)]^-$ which is obtained as the crystalline potassium salt from $SbCl_5$ and potassium azide in liquid SO_2 [327]. The complex dissolves in water with hydrolysis and in polar organic solvents.

9. Azides of Bismuth

The only two known azides of this element are of the organyl element type R_2BiN_3. Explosive properties have not been noted, but the compounds are, in accordance with the chemical periodicities noted earlier, less stable than the respective azides of Pb(IV) in the preceding group IVA. $(CH_3)_2BiN_3$ is obtained as colorless needles when trimethyl bismuth is reacted with ethereal hydrazoic acid; the compound decomposes above 150°C [$Pb(CH_3)_3N_3$, 200°C] [323]. The liquid $(C_6H_5)_2BiN_3$ is made by shaking for 60 hr the respective chloro compound with sodium azide in pyridine; it decomposes above 135°C [$Pb(C_6H_5)_3N_3$, 200°C] [324,328].

N. AZIDES OF THE VIA ELEMENTS

Our knowledge of the VIA azides is still fragmentary. The few compounds known, however, again show evidence of the periodicities typical of the preceding A groups; thus, the thermal stability of organyl element azides decreases from silicon to sulfur (Table XVI). Reichle [324] interprets this as a variance in the element-to-azide bond, $-\ddot{N}-\ddot{E}l-$; multiple bond formation is strongest in the Si case with five 3*d* orbitals unoccupied, while in groups VA and VIA one 3*d* orbital is used for O—P binding and two for O—S—O binding, respectively.

1. Azides of Sulfur

Sulfuryl azide,

$$N_3-\overset{\overset{O}{\vdots}}{\underset{\underset{O}{\vdots}}{S}}-N_3$$

is the parent compound for azides with sulfur-to-azide bonds. It was made in 1922 by Curtius and Schmidt [329] by shaking a suspension of sodium azide in sulfuryl chloride for 24 hr. Upon addition of water, sulfuryl azide separated as a colorless oil which tended to explode spontaneously.

Also known is a disulfuryl azide, $N_3-SO_2-O-O_2S-N_3$ [330], which was isolated as one of the end-products from reacting dry potassium azide with

Table XVI. Thermal Stabilities of Group IVA Through VI[a] Aryl Element Monoazides

IVA	VA	VIA
C $Ph_3C(N_3)$[a] Thermal dec., 190°C		
Si $Ph_3Si(N_3)$; Thermal dec., 380°C	P $Ph_2P(O)(N_3)$, Thermal dec., 140°C	S $PhS(O_2)(N_3)$; Thermal dec., 135°C
Ge $Ph_3Ge(N_3)$; Thermal dec., 375°C		
Sn $Ph_3Sn(N_3)$; Thermal dec., 300°C		
Pb $Ph_3Pb(N_3)$; Thermal dec., 200°C		

[a] Ph = phenyl.

sulfur trioxide gas. The liquid (MP, 17°C) explodes at 80°C and hydrolyzes in an exothermic reaction which may accelerate into explosion. The only known organylsulfur azide, $(C_6H_5)-O_2S-N_3$ (Table XVI), is accessible from sodium azide and benzenesulfonic chloride [9].

Another related compound is azidosulfonic acid, $HO-O_2S-N_3$. The potassium salt is made from hydrazinesulfonic acid and nitrite and is described as a water-soluble, crystalline solid which decomposes thermally with explosion [331].

2. Azides of Tellurium

Two mixed Te(IV) azides are known, namely, tellurium trichloride azide, Cl_3TeN_3 [332], and tellurium dichloride diazide, $Cl_2Te(N_3)_2$ [333]. Both compounds melt near 60°C and explode on heat shock and impact. The diazide is the less stable of the two, exploding at 130°C and, at times, spontaneously at room temperature. The compounds are made at room temperature by reacting tellurium tetrachloride with trimethylsilyl azide in dichloromethane media

Table XVII. Azide Chlorides of IVA through VIA Elements

Element	Group	Formula	Structure
Sn	IVA	$Cl_2Sn(N_3)_2$	Polymeric
Sb	VA	$Cl_4Sb(N_3)$	Dimeric
Te	VIA	$Cl_3Te(N_3)$	Monomeric

[333]. Infrared data suggest a monomeric, covalent structure which corresponds with a tr in other mixed azides (see Table XVII).

O. AZIDES OF GROUP VIIA

Azides of the higher oxidation states of the halogens are not known, leaving discussion to the four normal azides FN_3, ClN_3, BrN_3, and IN_3. The element-to-azide bonds are covalent, and no stabilization due to d_π-p_π electron interaction is noticeable; hence, these azides are extremely sensitive to decomposition. Nevertheless, the three heavier ones have found use in organic syntheses because the azide group is transferred easily either as radical or ionic processes. The halogen azides are in these cases reacted *in situ* as diluted solutions. All four halogen azides are photosensitive. They dissolve in organic solvents but tend to react slowly with nitrogen evolution, even when kept in the dark. Thermal and explosive sensitivities are listed in Table XVIII.

Of all known normal azides including HN_3, fluorine azide appears to be the most sensitive. The greenish-yellow gas was obtained in a nitrogen or argon environment at low temperatures. Slow mixing of diluted (1:200) fluorine and HN_3 yielded the azide, apparently according to [334]:

$$4HN_3 + 2F_2 \longrightarrow 3FN_3 + NH_4F + N_2$$

Fast mixing produces mainly F_2N_2 [339].

Chlorine azide tends to explode spontaneously even at reduced pressure. Mixtures with inert gases appear to be more stable but are still sensitive to mechanical or thermal shock. Solutions in organic solvents have shelf lives of several days at room temperature and in the dark [335,336].

Chlorine azide gas is prepared [336,340] in acid media according to:

$$N_3^- + ClO^- + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} ClN_3 + 2OH^-$$

Acetic and boric acids are useful for the process as they react without gaseous by-products. Mineral acids liberate hydrazoic acid and thus contaminate the

Table XVIII. Properties of the VIIA Azides

		Slow decomposition	Explosive sensitivity	References
FN_3	MP, −154°C BP, −82°C	Room temperature, at 200 mm Hg	Vaporization causes explosion	336
ClN_3	MP, −45°C BP, 15°C	Room temperature	Spontaneous explosions at room temperature	335, 336
BrN_3	MP, −45°C	Room temperature	Spontaneous explosions	337
IN_3	solid	Room temperature	Slight mechanical and thermal shock	338

product. The reaction takes place in a flask containing the acid; equimolar solutions of sodium azide and hypochlorite are mixed and added thr a dropping funnel. A stream of nitrogen carries the product out. The above method has only recently been replaced [10,140] by a simple and efficient process:

$$Cl_2 + NaN_3 \longrightarrow ClN_3 + NaCl$$

A chlorine/nitrogen mixture (1:1) at 0°C is bubbled into an aqueous solution of sodium azide; the evolving gases may be dried with P_2O_5.

Bromine azide is an orange liquid of equally treacherous properties. Spencer made the compound in 1925 [337] from bromine/nitrogen mixtures and dry sodium azide (BrN_3 hydrolyzes instantly in water) and noted its "pungent but sickly" smell and its extreme sensitivity to mechanical and thermal shock. A third of his attempts to establish the melting point (−45°C) ended with explosion, "reducing the apparatus to powder." The compound is, even at reduced pressure, highly sensitive to pressure fluctuations; Dehnicke [10] found a pressure of 0.05 mm Hg sufficient to cause an explosion. Hassner and Boerwinkle [341] have used BrN_3 *in situ* in dichloromethane/pentane media at 0°C for stereospecific syntheses. Solutions of the compound in organic solvents are photosensitive and decompose within hours.

Equally noxious and sensitive is the solid iodine azide which was made in 1900 by Hantzsch [338] from iodine and silver azide in water/ether media; the product collected in the ether layer. Hassner and coworkers [342,343,344] made it from sodium azide and iodine chloride, ICl, in ice-cold solvents such as acetonitrile or dichloromethane; a little water is required for the reaction. The product was employed *in situ* to transfer the N_3 group to organic molecules.

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The Growth of Crystals

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A. INTRODUCTION

The growth of large single crystals of many metals and salts has proven to be a significant development for the characterization of their physical properties. Materials in single-crystal form have also found direct technological application, especially in the electronics and electro-optics industries. The progress of azide research, especially in understanding the solid-state physical properties, has greatly benefited from the use of good-quality single crystals and thin films. In particular, the availability of crystals and thin films of azide compounds has led to a more detailed understanding of the electronic and lattice structure, the lattice dynamics, and the decomposition process.

As a class, the azides present several problems when attempting to use the well-known techniques of crystal and thin-film growth. Their instability conflicts with the successful application of most "thermal" approaches, and their restricted solubilities limit the usefulness of growth from aqueous solutions. For instance, growth by sublimation techniques is not feasible because the azide ion decomposes at elevated temperatures. Melt growth is limited to the azides of K, Rb, Cs, and Tl, of which only KN_3 is sufficiently stable at its melting point to permit routine success. Thus, while the azides must, in general, be crystallized from solutions, precautions are also necessary to avoid hydrolytic decomposition when water is used as the solvent.

The following general techniques for inducing solubility changes in solution have been applied to the growth of azide crystals:

1. Solvent evaporation: temperature constant, volume decreased
2. Slow cooling: volume constant, temperature decreased